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## XVIII. *The Specific Heat of Iodine.* *By* L. G. CARPENTER *and* T. F. HARLE, *The Physical Laboratory, University College, Southampton* *.

### *Introduction.*

THE variation with temperature of the specific heat of solids and liquids is of theoretical interest, for it throws light upon the motion of the atoms and the forces which act upon them. At low temperatures quantum conditions control the phenomena, as generally the energies thermally available are small compared with the minima which are demanded by quantization. Although it is true that at higher temperatures quantum conditions are usually no longer restrictive and behaviour can be interpreted in terms of classical mechanics, nevertheless the phenomena acquire a new interest, since the thermal forces become comparable with the lattice forces and eventually lead to lattice breakdown, *i. e.*, melting. The state of affairs in the liquid phase after melting is particularly worthy of study, since little is known of the temperature variation of specific heats of liquids and there is as yet no satisfactory theory.

The present work forms part of a programme of investigation of the specific heat of the elements at high tempera-

* Communicated by the Authors.

tures and in the liquid phase. As the point of interest is the variation of specific heat with temperature it is, of course, desirable to measure the true specific heat over small ranges of temperature rather than the average over large temperature ranges, although the latter has hitherto been more usually done.

When the temperature is high enough to make quantum conditions no longer restrictive, but yet not so high as to make the atomic oscillations anharmonic, $C_v$, the specific heat per gram atom at constant volume, should be 3R if the heat content of the electrons does not vary with temperature, *i. e.*, if the specific heat of the electrons is negligible. It is therefore of interest to measure $C_v$ for a substance which is an insulator. Iodine was chosen because it was found that no data on its true specific heat above 200° K. were available. It is easily obtainable in a pure form, and melts at a relatively low temperature (114° C.), so that it was possible to investigate it right into the liquid phase. Moreover, for the solid the data for the calculation of the theoretically interesting $C_v$ from the observed $C_p$ (atomic heat at constant pressure) are available.

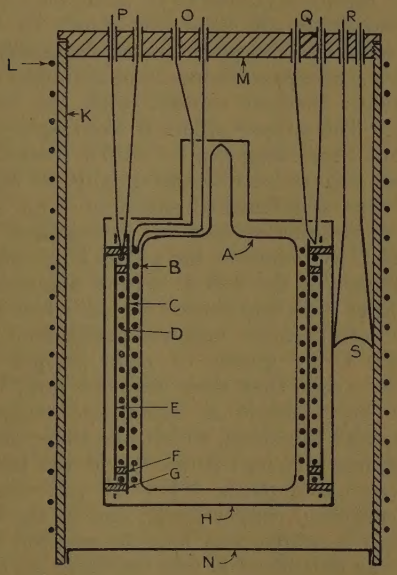
*Apparatus and Experimental Procedure.*

The measurement of the specific heat of solid and liquid iodine presents several problems of unusual difficulty. Its vapour pressure is high, and it must therefore be enclosed in a gas-tight vessel which must be non-metallic, since iodine reacts with all the suitable metals. If a glass or silica container is employed the solid iodine must be used in the granulated form, as we found that, if an attempt is made to cast it inside the vessel, the vessel cracks on cooling. Unfortunately the use of granulated material means that the ratio of heat capacity of iodine to that of container becomes lower than is desirable, unless especial care is taken to keep down the thermal capacity of the container. Moreover, the cracking of the vessel, which we found to occur on solidifying the melt, demands that, once the iodine has been melted, in order to make measurements on the liquid phase it must be kept molten until all the desired measurements have been made.

The thermal conductivity of solid iodine is low (about $1 \times 10^{-3}$), and the effective conductivity of the granulated

material still lower, so that special precautions have to be taken to ensure that the temperatures which are measured are really representative of the whole mass of the iodine. After a considerable amount of experiment a design of calorimeter was adopted which, though following the general lines of an earlier paper *, introduced important modifications of detail. Briefly, the calorimeter vessel consisted of a sealed pyrex vessel in a light metal container, the contact between the two being

Fig. 1.




made by bakelite varnish. The construction is shown diagramatically in fig. 1, which is not drawn to scale. The pyrex vessel A was 8 cm. long, 4 cm. in diameter, and of wall thickness about 1 mm. The outer surface of A was etched by hydrofluoric acid, and then covered by thin silk fabric attached by bakelite varnish, on which was wound 100 ohms of 30 S.W.G. manganin wire B,

* Carpenter and Harle, Proc. Phys. Soc. xliv. p. 383 (May 1932).

more bakelite varnish being applied, together with an outer coat of thin silk fabric. While the bakelite was still tacky a piece of $2\frac{1}{2}$ mil copper foil C (to which two sets of copper pillars F and G had already been attached with cadmium-zinc solder) was wrapped round and secured by a touch of the solder. C was perforated by circular holes of about 3 mm. diameter, which facilitated the evaporation of solvent from the bakelite varnish and also allowed more varnish to be introduced where necessary. A coil D of 3·3 metres of 40 S.W.G. (bakelite covered) pure platinum wire was wound on top of the copper foil C, but was not rigidly attached to it, being kept in place by guides of bakelized silk fibre not shown in the figure. Thus D, which was the platinum thermometer coil, was mounted in a strain-free manner, and radiation provided * quite adequate thermal contact with the rest of the calorimeter. The copper pillars F were eight in number and were each 4 mm. long and 3·5 mm. in diameter. They were drilled and tapped longitudinally to take 8 B.A. screws. E was a cylindrical shield of 4 mil silver foil, blackened on its inner surface and maintained in thermal contact with C by means of the pillars F, to which it was bolted by means of the 8 B.A. screws mentioned above. H was an outer radiation shield of 4 mil silver foil, highly polished on both surfaces, and was maintained in thermal contact with C by means of eight copper pillars G, similar to F except that they were 6·5 mm. long. The calorimeter hung inside a cylindrical copper mantle K of 3 mm. wall thickness, which was silver-plated on its inner (calorimeter facing) surface, and the mantle hung inside an evacuated pyrex tube. K was closed at the top by a screwed-in copper lid M, and at the bottom by a silver plate N which was held in position by 8 B.A. bolts. On the outside of K was bakelized an iron coil L, consisting of 14 metres of 26 S.W.G. wire, the advantage of using iron being that L could be used as a rough resistance thermometer. Three differential copper constantin (40 S.W.G.) thermocouples were connected in series between the calorimeter and the mantle (only one is shown at S), and connected by means of the leads R to a potentiometer. The pairs of leads marked P and Q go to the platinum resistance and compensating sides of a

* *Vide* Carpenter and Harle, *loc. cit.*

Callendar Griffiths bridge, while O goes to the circuit for electrical heat input. The fact that the silver shields H and E and the copper foil C were bolted firmly together by means of copper pillars G insured that they were all at the same temperature. The thermometer coil D was also at the same temperature, since its bakelite covering was effectively a black body radiator, and it was enclosed in a black body annular space formed by the blackened inner surface of E and the bakelized silk outer surface of C. Hence the thermometer coil could be relied upon to give the temperature of the metal part of the calorimeter.

In preliminary experiments the calorimeter (without the differential couples S) was used in the usual way, *i. e.*, the temperature of the calorimeter was measured by means of the thermometer coil D, a known quantity of heat put in by the heating coil B, keeping the mantle K at constant temperature, and finally the temperature of the calorimeter was again measured by means of the thermometer coil, making what correction was necessary for the heat loss during the experiment. It was feared, however, that the very poor thermal conductivity of the granulated iodine would introduce an error in the following way. Suppose, for example, that at the beginning of an experiment the temperature of the mantle was equal to that of the metal foils C, E, and H of the calorimeter. In these circumstances there is no doubt that the temperature of the iodine is that given by the thermometer coil D. Now imagine that, by means of the heating coil, enough heat is put into the calorimeter to raise the temperature of metal, pyrex, and iodine by (say) 1° C. The metal part of the calorimeter being now 1° above the mantle there is a flux of heat outwards from the calorimeter. Owing to bad thermal conductivity the iodine is then hotter than the outer metal parts of the calorimeter, and hence the measured rise of temperature is too low and the deduced heat capacity too high. In view of the above possibility of error it was decided to introduce the differential couples S and to work under adiabatic conditions, heating the mantle by means of the iron heating coil K, while the calorimeter was heated by B in such a way that the temperature difference between K and the calorimeter was maintained at zero throughout the experiment. All the results given in this paper were obtained under

adiabatic conditions. However, some preliminary experiments were made using the ordinary non-adiabatic method, and it was found that, while the results obtained by the two methods agreed at low temperatures and at room-temperature, at about +50° C. the non-adiabatic experiments gave results about 1 per cent. higher than the adiabatic ones, the sign of the difference being what one would expect. It is not possible to compare the two methods at higher temperatures, as no non-adiabatic experiments were done above 50° C.

In order to facilitate heat conduction through the granulated iodine helium was introduced at about 10 mm. pressure and the pyrex container sealed off. In addition, when filling, pieces of 20 S.W.G. tungsten wire coated with pyrex were introduced between the grains of iodine, in the hope that the tungsten wire, on account of its relatively high thermal conductivity (0·48), might aid the attainment of thermal equilibrium throughout the mass.

The heat input by means of the manganin coil B was measured with an accurately calibrated voltmeter and milliameter and a standard clock, and the rise of resistance of the platinum coil D with a Callendar Griffith bridge. The $\alpha$ and $\delta$ of the Callendar's platinum resistance formula were determined by calibrations at the ice-point, the steam-point, and the freezing-point of Kahlbaum's pure tin, and were $39{\cdot}20 \times 10^{-4}$ and 1·535 respectively.

The pyrex tube in which the apparatus was suspended was evacuated by an 02 Burch oil-vapour pump backed by a mechanical pump, and was placed in an electric furnace with a muffle of copper. The furnace temperature was maintained constant to a tenth of a degree Centigrade by a modified Cooke and Swallow * platinum resistance thermostat, the modification consisting of the replacement of the Weston relay by a moving coil galvanometer, photocell, and single stage valve amplifier. For work below room-temperature baths of ice and of solid carbon dioxide were used.

It was found that, owing to the difference in temperature between the lid M and the mantle K (K being hotter than M when working above air-temperature, and colder than M when working below air-temperature), the heat

* J. Sci. Inst. vi. p. 287 (1929).

interchange between the calorimeter and its surroundings was not a unique function of the e.m.f. developed by the three differential thermocouples S in series. It resulted that, if this e.m.f. had a certain value when the calorimeter was (say) gaining heat at a certain rate, and if the temperature of the calorimeter were raised by 1°, then it was necessary to increase the temperature of the mantle to an extent such that the reading of the differential thermocouples was slightly greater than before, in order that the rate of gain of heat of the calorimeter should be unaltered. The amount that the e.m.f. of the differential thermocouples had to be increased in order that the rate of heat exchange should not be altered was determined by experiment. It was greater the higher the temperature of the calorimeter above that of the room.

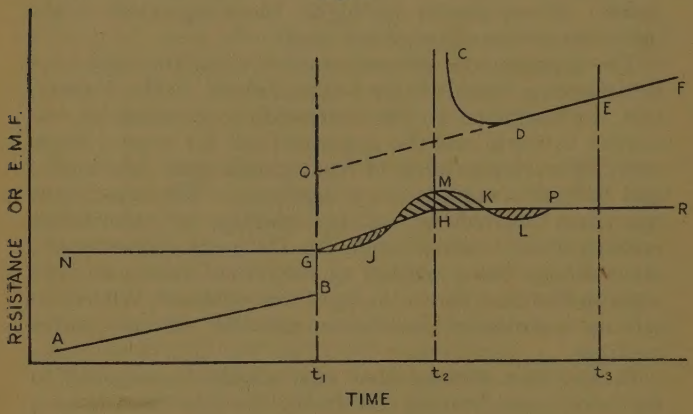
The experimental procedure when using the apparatus to determine specific heats was as follows :—The thermostat was adjusted to the temperature at which it was desired to work, and the apparatus left for several hours until the temperatures of the mantle and calorimeter had become steady, or very nearly so. The experiment was then started by taking readings of calorimeter resistance and thermocouple e.m.f.'s every five minutes, the readings being plotted as they were taken, so that a graph like that shown in fig. 2 was obtained, AB representing calorimeter resistance and NG thermo-couple readings.

It was then decided that heat should be supplied to the calorimeter heating coil during the time from $t_1$ to $t_2$ at a certain rate, thus producing a certain rise of calorimeter temperature. From previous experience it was known that, if the slope of the calorimeter resistance/time curve was to be the same after the heat input as before, the thermocouple e.m.f. must be increased by a definite amount. The (ideal) thermocouple line GHR was therefore drawn, the difference between the ordinates of H and G being the definite amount just mentioned.

At time $t_1$ the currents in the calorimeter heating coil B and the mantle heating coil L were switched on, the thermocouple readings taken and GJM plotted. At time $t_2$ the calorimeter heating current was switched off. If conditions had been truly adiabatic during the heat input the actual thermocouple curve GJM would have been such that the area between it and the time

axis was equal to the area between GH and the time axis. In general, however, this was not so, and hence during the period subsequent to $t_2$ the thermocouple curve MKLPR was plotted, and the mantle heating current varied until exact equality of the two areas was obtained. This meant in practice the equality of the right-to-left and left-to-right shaded areas in fig. 2. Observations were continued until a time $t_3$, such that it was certain that the whole of the calorimeter was at the temperature indicated by the coil resistance E. From $t_3$ onwards the line EF was straight and parallel to AB if the thermocouple

Fig. 2.




e.m.f.'s were maintained at the proper value by manipulation of the mantle heating current. The straight line FE was extrapolated backwards to cut the $t_1$ ordinate at Q, and QB was then the rise of temperature of the calorimeter due to the heat input during $t_2-t_1$, no further heat loss correction being necessary. A slight correction to the calorimeter heat input, as calculated from milliamperes, volts, and time, was made to allow for the heat developed in the leads. This was about $\frac{1}{4}$ per cent. The weight of the empty calorimeter assembled complete with its silver radiation shields was 111·00 grams, and it contained 176·95 grams of iodine in the form of thin flakes of average diameter about 3 mm. The iodine was Hopkin and Williams's AR grade, and has been

specially resublimed over potassium iodide. It appeared to be of a high degree of purity, two separate gravimetric estimations both giving 99·81 per cent. of iodine by weight. The residue on ignition was nil, and iodine cyanide was found to be absent. It is reasonable to suppose that most of the remaining 0·19 per cent. was water.

In order to compare the mean specific heat of iodine obtained over the range 100° C. to air-temperature by the method of mixtures with the average of the true specific heat over the same range 136·42 grams of the same stock of iodine were sealed in a pyrex vessel (weight 27·25 grams), air at nearly atmospheric pressure being allowed to remain to facilitate the attainment of thermal equilibrium. The calorimeter was of the design usual in the method of mixtures, the calorimetric liquid being water. As it was necessary to wait about 25 minutes before the pyrex vessel and contained iodine had attained the temperature of the water special attention was paid to the correction for heat exchange between the calorimeter and its surroundings, which were maintained at a uniform and known temperature. All necessary precautions were taken and carefully standardized thermometers used.

The results obtained varied rather widely among themselves, probably on account of the difficulty of the poor thermal conductivity mentioned above. The question will be discussed in the next section.

### *The $C_p - C_v$ Correction.*

The value of $C_p - C_v$ at 20° C. was calculated from the thermodynamic formula

$$C_p - C_v = \frac{9\alpha^2 VT}{\kappa}, \quad \ldots \ldots \quad (1)$$

where $\alpha$, V, T, and $\kappa$ are the coefficient of linear expansion, the molecular volume, the absolute temperature, and the compressibility respectively.

Taking $\alpha$ as $93 \times 10^{-6}$ *, the density as 4·93 *, the atomic weight as 126·93, and $\kappa$ as $13{\cdot}0 \times 10^{-12}$cm.$^2$/dyne†, one gets

$$C_p - C_v = 1{\cdot}081 \text{ cals./gram atom/°C. at } 20° \text{ C.}$$

* 'International Critical Tables,' i. p. 104.
† T. W. Richards, J. A. C. S. xxxvii. p. 1646 (1915).

Unfortunately the variations of $\alpha$ and $\kappa$ with temperature are not known. It is therefore necessary to use the approximate formula which assumes that $\alpha$ is proportional to $C_p$ and that $V/\kappa$ is a constant.

Then

$$C_p - C_v = AC_p^2T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and inserting the value for 20° C., $C_p - C_v$ can be calculated over the whole temperature range of the solid phase.

In Table I. the results of this calculation are given. Unfortunately it is not possible to calculate $C_p - C_v$ for liquid iodine, because the compressibility is not known. A lower limit can, however, be obtained in the following

TABLE I.

$C_p - C_v$ for Solid Iodine.

| Temperature in °K. | $C_p - C_v$ per gram atom. |
|---|---|
| 30 | 0·028 |
| 50 | 0·084 |
| 70 | 0·147 |
| 110 | 0·282 |
| 150 | 0·428 |
| 230 | 0·764 |
| 293 | 1·081 |
| 350 | 1·410 |
| 385 | 1·637 |

way. The compressibilities of liquid chlorine and bromine at 20° C. are given by Richards * as $95 \times 10^{-6}$ and $52 \times 10^{-6}$ respectively, when the pressures are measured in megabars. The compressibility of liquid iodine is very unlikely to be greater than that of liquid chlorine, and hence we shall get an upper limit to $C_p - C_v$ if we take $\kappa$ as $52 \times 10^{-12}$ cm.$^2$/dyne.

If we make the calculation of $C_p - C_v$ for the temperature 120° C. we have † a cubical expansion coefficient of $8{\cdot}2 \times 10^{-4}$ and a density of 3·95. Hence

$$C_p - C_v = 3{\cdot}90 \text{ calories/gram atom}$$

as a lower limit.

* *Loc. cit.*

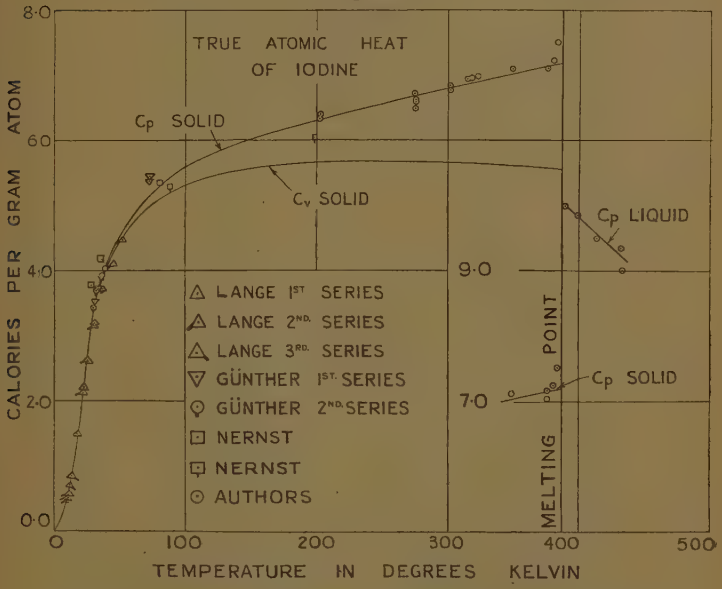
† Nayder, *Acad. Polonaise Sci. et Lettres Bull.* v.–vii. A, p. 231 (1934) also I. C. T. iii. p. 20.

*Experimental Results.*

The experimental values of $C_p$, the heat capacity per gram atom at constant pressure, are given in Table II. They were obtained by subtracting from the individual experimental values of the heat capacity of the full calorimeter the corresponding values for the empty calorimeter as read from a smooth curve.

It was necessary to make a small correction for the vaporization of iodine into the part of the calorimeter

Fig. 3.




which it did not fill, using the known vapour pressure curve and latent heat of vaporization of iodine *, and calculating the space available for evaporation from the mass and density of iodine and from the volume of the calorimeter. This correction amounted to 3·5, 1·2, and 0·4 per cent. of the heat capacity of the iodine at 160°, 100°, and 75° C. respectively.

* The vapour pressure curve was taken from I. C. T. iii. p. 201, and the latent heats of vaporization of solid and liquid from Newton Friend's 'Text-book of Inorganic Chemistry,' viii. p. 199.

The heat capacities were converted to atomic heats, using a value of 126·932 for the atomic weight of iodine. In fig. 3 the values of Table II. are plotted, together with the results of Nernst, Lange, and Günther *, and a continuous curve has been drawn in the way which seems best to represent the results of all observers. The rapidly increasing rise in the 10° immediately preceding

TABLE II.

Experimental Values of $C_p$ for Solid and Liquid Iodine.

| Temperature in °K. | $C_p$ per gram atom. |
|---|---|
| 202·2 | 6·35 |
| 202·9 | 6·41 |
| 274·6 | 6·74 |
| 275·1 | 6·50 |
| 275·3 | 6·64 |
| 275·5 | 6·60 |
| 301·5 | 6·78 |
| 301·9 | 6·85 |
| 314·8 | 6·95 |
| 318·0 | 6·97 |
| 322·8 | 7·00 |
| 348·7 | 7·11 |
| 375·7 | 7·12 |
| 380·3 | 7·24 |
| 383·2 | 7·51 |
| 387·1 | melting-point. |
| 389·4 | 10·00 |
| 398·8 | 9·86 |
| 413·2 | 9·50 |
| 431·9 | 9·35 |
| 432·7 | 9·01 |

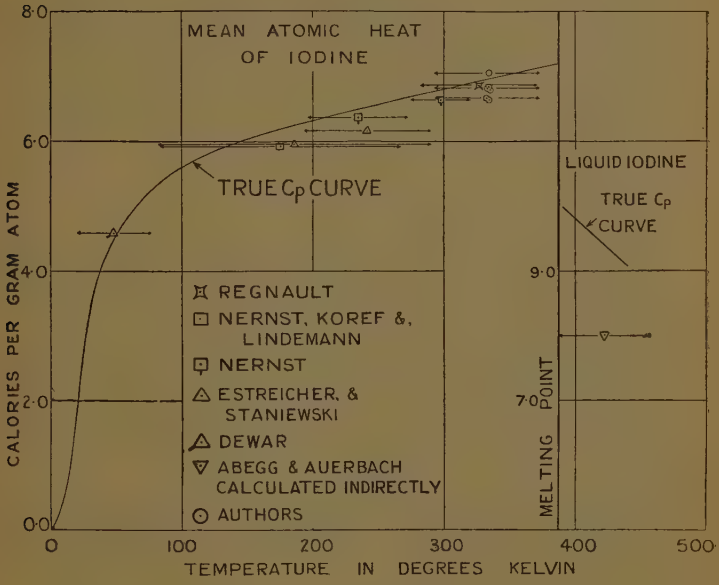
the melting-point has been ignored in drawing the smooth curve, as it is known that exceedingly small amounts of impurity will produce such effects †.

* Nernst, *Ann. der Phys.* (4) xxxvi. p. 395 (1911), and *Berlin. Sitzber.* xii. p. 262 (1910) ; Günther, *Ann. der Phys.* (4) li. p. 828 (1916) ; Lange, *Zeits. f. phys. Chem.* cx. p. 343 (1924). Below 30° K. Günther found considerable scatter in his experimental values, attributed by him to a slow transformation which Lange was unable to confirm. As Lange made three series of observations, which are all concordant, we have plotted these in fig. 3 and omitted Günther's points below 30° K.

† *Vide*, *e. g.*, Carpenter and Harle, Proc. Roy. Soc. A, clxiii. p. 243 (1932), where it is shown that 0·014 atomic per cent. of impurity known to have been present quantitatively accounts for the very large effect in bismuth near its melting-point. See also Carpenter, Trans. Far. Soc. xxix. p. 1083 (1933).

By subtracting the values of $C_p - C_v$ given in Table I. the values of $C_v$ have been obtained; these are also plotted in fig. 3. It is difficult to give an estimate of the accuracy of the measurements of $C_v$, but probably the greatest uncertainty arises in the elimination of the radiation loss by the adiabatic method described above. However, it is unlikely that the inaccuracy of the results due to all causes combined amounts to more than 3 per cent.

Fig. 4.




Six measurements of mean specific heat taken over the range from 100° C. to 20° C. were made, the resulting values for $C_p$ (the mean temperature being about 335° K.) being 6·81, 6·66, 6·84, 7·05, 6·64, and 6·79.

The scatter of the results is rather large, and the mean, viz. 6·80, is about 3 per cent. lower than the value (7·02) of the true specific heat derived from the curve in fig. 3.

We have been unable to account for this discrepancy. In view of the close agreement at 50° C. (within 1 per cent.) of the non-adiabatic and adiabatic measurements

(in which the methods of heat loss correction are quite different) it is improbable that there is much wrong with the true specific heat measurements, especially as the other quantities involved in them, viz., energy input and rise of calorimeter temperature, are very unlikely to be seriously affected by experimental error.

Hence the discrepancy, if due to error in the measurements, is probably to be attributed to error in the mean specific heat results. The question as to whether the discrepancy may be real is discussed in the next section.

In fig. 4 the results of our mean specific heat measurements have been plotted, together with those of other observers *, the range of temperature appropriate to each mean value being indicated by horizontal lines. The continuous curve of true specific heats has been copied for comparison from fig. 3.

*Discussion of Results.*

The $C_v$ curve in fig. 3 is of the usual general form, but unfortunately it is not profitable to compare it with that given by Debye's theory, as according to Harris, Mack, and Blake the iodine lattice is diatomic †. Certain general conclusions can, however, be drawn from the higher temperature region of the curve. It is noteworthy that right up to within 10° of the melting-point $C_v$ does not exceed 3R, and, as mentioned above, the increase in the immediate neighbourhood of the melting-point is probably due to impurity.

While the variation of the $C_p - C_v$ correction with temperature may not be given quite accurately by equation (2), there can be no doubt that the value is substantially correct at 20° C. On the other hand, the value of $C_p$ at this temperature can hardly be too low; indeed, if anything it is (having regard to the lower values obtained for the mean specific heat by the method of mixtures) too high. Hence we may conclude with considerable certainty that at room-temperature $C_v$ is not greater than 6 calories per gram atom, and in view

* The values given are taken from Landolt-Börnstein's *Physikalisch-chemische Tabellen*, ii. 5th edition (1923), together with a value of Regnault for the solid, and a value for the liquid calculated indirectly from thermodynamical data, both the latter being given in vol. viii. of Newton Friend's ' Textbook of Inorganic Chemistry.'

† J. A. C. S. l. p. 1583 (1928).

of the fact that equation (2) is at least approximately correct we may be reasonably certain that even at the melting-point $C_v$ does not exceed 6 calories by much, if at all.

At room-temperature and higher, the quantum condition associated with the binding of the two atoms in the molecule does not prevent the equipartition value of thermal energy being practically attained, since, if we take the value $\frac{h\nu}{k}=300$, which is appropriate to the gaseous molecule * (and the binding in the solid will be if anything looser than this) at 300° K., the Einstein function becomes about 5·5 calories per gram atom. The curve of $C_v$ against temperature appears from fig. 3 to pass through a flat maximum at about 300° K. and then to decrease slightly on approaching the melting-point. Though it is not possible, on account of uncertainty as to the variation of the $C_p-C_v$ correction with temperature, to attach much importance to this slight maximum, its existence is by no means theoretically impossible. If the atomic oscillations become anharmonic when large, $C_v$ will decrease with temperature if the departure from harmonicity is in the direction of the restoring force increasing more than linearly with the displacement. According to Eucken and Dannöhl † sodium chloride and silver both show the phenomenon of a maximum in $C_v$ followed by a slow decrease.

It has already been mentioned that the average value of the mean specific heat results for the solid from 100° C. to room-temperature is about 3 per cent. lower than the true specific heat. This discrepancy may be due to experimental error, but it is not impossible that it is real and significant.

The two sets of measurements were made under different conditions, as in the "mean" experiments the iodine was suddenly cooled down from 100° C. to room-temperature, while in the "true" experiments it was heated about 1° during a period of several minutes. Now it is a well-known property of certain metals that specimens which are suddenly cooled do not immediately attain the energy state corresponding to the lower temperature.

* Cox, Proc. Camb. Phil. Soc. xxi. p. 544 (1923).
† *Zeits. f. Elektrochem.* xl. 11, p. 789 (Nov. 1934).

If this effect were present here the specific heat as measured by cooling the iodine would be less than that obtained by heating it. Further, it has been suggested by Kurbatoff * that there are two modifications of iodine with a transition point at about 47° C. However, we found no indication of this in the present work, and there does not seem to be any difference in specific heat above and below this temperature.

The value of $C_p$ for the liquid phase is of the order of 10 calories per gram atom, and decreases fairly rapidly with temperature. Since the lower limit of $C_p - C_v$ for the liquid is about 3·9 calories, $C_v$ cannot exceed 3R much, if at all. Hence one may conclude (as indeed is to be expected) that the number of degrees of freedom in the liquid does not exceed the number in the solid.

3rd July, 1936.

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XIX. *A Note on the Dependence of the Mobility of Ions in Pure Gases on Temperature.* *By* L. G. H. Huxley, *M.A., D.Phil., F.Inst.P., University College, Leicester* †.

In two recent papers Professor A. M. Tyndall and Mr. A. F. Pearce ‡ have given results of reliable measurements of the variation with temperature of the mobilities of various ions in pure gases, and they also discuss their results in relation to the rigorous theoretical investigations of Langevin and of Hassé and Cook §.

In Langevin's investigation the ions and molecules are treated as elastic spheres, and in those of Hassé and Cook as point-centres of force repelling mutually with a force varying as the inverse ninth power of the distance. In both cases the effect of the polarization of the molecules by the ions is represented by an additional inverse fifth-power force of mutual attraction.

According to Tyndall and Pearce the experimental results suggest that better agreement with theory would

* *Zeits. anorg. Chem.* lvi. p. 230 (1907).

† Communicated by the Author.

‡ A. M. Tyndall and A. F. Pearce, Proc. Roy. Soc. A, no. 868, cxlix. p. 426 (April 1935), and A. F. Pearce, Proc. Roy. Soc. A, no. 886, clv. p. 490 (July 1936).

§ P. Langevin, *Ann. Chim. Phys.* v. p. 245 (1905); Hassé, Phil. Mag. i. p. 139 (1926); Hassé and Cook, Phil. Mag. xii. p. 554 (1931).

be obtained on the hypothesis of point-centres of force repelling according to an inverse power of the distance greater than nine but less than infinity.

Nitrogen Ions in Nitrogen.

A=252 ; C=1325.

| T° abs. | $k_\rho$ obs. | $k_\rho$ calc. |
|---|---|---|
| 587..... | 3·19 | 3·21 |
| 500..... | 3·11 | 3·09 |
| 407..... | 2·94 | 2·94 |
| 292..... | 2·67 | 2·66 |
| 169..... | 2·15 | 2·18 |
| 90..... | 1·62 | 1·69 |
| 77..... | 1·56 | 1·57 |
| 65..... | 1·46 | 1·46 |

Cæsium Ions in Helium.

A=543 ; C=200.

| T° abs. | $k_\rho$ obs. | $k_\rho$ calc. |
|---|---|---|
| 492..... | 17·4 | 17·4 |
| 392..... | 18·1 | 18·2 |
| 290..... | 18·9 | 18·9 |
| 195..... | 19·2 | 19·2 |
| 92..... | 18·0 | 17·9 |
| 79..... | 17·5 | 17·4 |

Sodium Ions in Helium.

A=1240 ; C=462.

| T° abs. | $k_\rho$ obs. | $k_\rho$ calc. |
|---|---|---|
| 477..... | 24·6 | 24·4 |
| 405..... | 24·0 | 24·0 |
| 290..... | 22·8 | 22·8 |
| 195..... | 20·9 | 20·8 |
| 92..... | 18·5 | 16·4 |

It is surprising to find that in some instances the experimental results are represented with great accuracy by a formula proposed by Sutherland to account for the effect on the mobility of the attractive forces of polarization.

Sutherland's formula, which is analogous to his well-known formula connecting the viscosity of a gas with

its temperature, is, however, derived by an approximate theory, so that it is best regarded as semi-empirical in status. According to Sutherland *, the mobility $k_\rho$ of an ion in a gas at normal density should be related to the absolute temperature T of the gas by the formula

$$k_\rho = \frac{AT^{\frac{1}{2}}}{C+T},$$

in which A and C are constants characteristic of the gas and the ion. C is clearly the temperature $T_m$ at which the mobility is a maximum.

A comparison is given above of the value of the mobilities measured by Tyndall and Pearce and the values calculated from Sutherland's formula when suitable values are assigned to A and C.

The results given for helium ions in helium indicate the same mobility, $k_\rho = 21{\cdot}4$ cm. per sec. per volt per cm., at the three temperatures absolute, 480°, 399°, and 291°, so that it is not possible to fit Sutherland's formula to them, although it seems probable that the apparent straight portion of the curve is actually a flat maximum.

My best thanks are due to Professor Tyndall and, through him, to Professor Hassé for helpful criticism.

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## XX. *Motions of Electrons in Gases in Electric and Magnetic Fields.*

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### I. *Introduction.*

In scientific literature dealing with the motions of electrons in gases, the formulæ used to express the mean velocity of drift W of a group of electrons in the direction of the electric force X are of the form

$$W = g.\frac{Xe}{m}\left(\frac{\bar{l}}{U}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $g$ is a numerical coefficient, $e/m$ the ratio of the charge $e$ of the electron to its mass $m$, and $\bar{l}/U$ the mean

* Sutherland, Phil. Mag. (6) xviii. p. 341 (1909).

† Communicated by the Author.

value of the ratio of the mean free path $l$ to the corresponding velocity of agitation U.

Although the coefficient $g$ has usually been considered as unity, its correct value is 2/3, and Townsend [1] has recently given two methods of deriving the accurate formula.

He shows that an error had been introduced into many previous derivations by neglect of the influence of the field on the time spent between collisions. This error is inherent also in analogous formulæ [2] which have been found for the velocity of drift W when the electric field is accompanied by a magnetic field.

As a study of the motions of electrons among molecules or atoms in the presence of a magnetic field is of importance for theories of the ionosphere [3], for the classical theory of the Hall Effect, and for experimental determinations of the velocities of drift W of electrons [11], [12], it is desirable to obtain the appropriate formulæ in their correct form.

Before proceeding to the investigation of the motions in a magnetic field, another method of establishing the correct value for the coefficient $g$ in equation (1) will first be given, as it serves to relate the processes of diffusion and drift of electrons with Maxwell's equations of diffusion which are used subsequently.

## II. *Motion in Absence of Magnetic Field.*

Consider an element of area $d$S, fig. 1, lying in the $xOy$ plane at the origin.

Let the number of electrons in any small volume be small compared with the number of molecules of the gas in the same volume, so that the only collisions which are of importance are those between electrons and molecules.

Suppose the number $n$ of electrons per unit volume to be given, in the steady state, over a plane $z=$constant, by

$$n=n_0+z\,.\,\frac{dn}{dz}=n_0+r\cos\theta\,.\,\frac{dn}{dz},$$

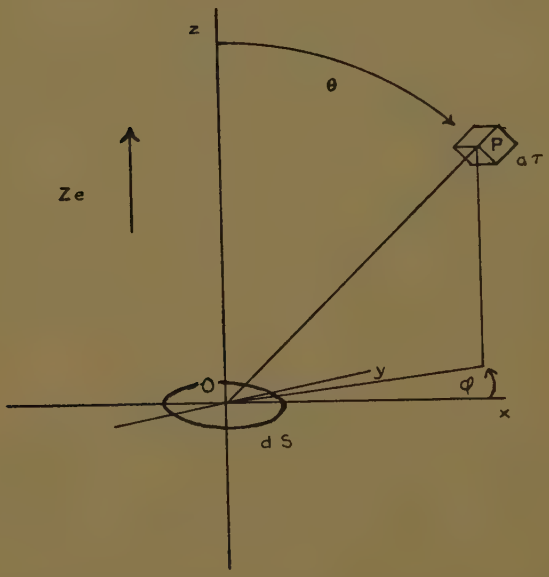
and the force $Ze$ on an electron to act along $Oz$ as indicated.

In order to calculate the net transport of electrons across $d$S per second in the direction $Oz$, consider an element of volume $d\tau=r^2\sin\theta d\phi d\theta dr$ at the point P$(r, \theta, \phi)$, and suppose, for the moment, that all electrons possess

the common velocity of agitation U. The number of electrons emitted from $d\tau$ per second within any small solid angle $d\omega$ is $\frac{nU}{l} \cdot \frac{d\omega}{4\pi} . d\tau$, and the number of these which reach a distance $r$, from $d\tau$ without collision, is

$$\frac{nU}{l} . e^{-r/l} \frac{d\omega}{4\pi} d\tau.$$

Fig. 1.



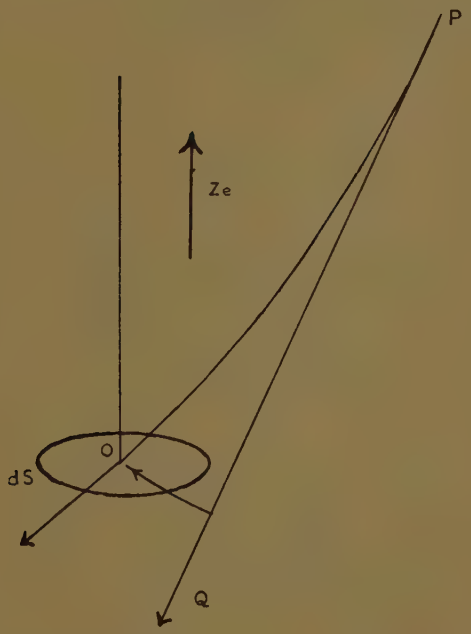

Consequently, the number of electrons which traverse $dS$ per second after colliding within $d\tau$, when the field is absent, is

$$\frac{nU}{l} e^{-r/l} \frac{dS \cos\theta}{4\pi r^2} . d\tau.$$

When an electric field Z is applied, the elementary beams of electrons issuing from $d\tau$ are deflected, so that the beam PO, fig. 2, which crosses $dS$ would, in the absence of Z, have travelled along PQ.

When the curvature of the paths in the field is slight, the distance travelled along the path PO from P to O is sensibly equal to the direct distance $r$, and the principal effect of the field, as far as transport of electrons across $d$S is concerned, is to change the angle of incidence of the beam at O, arriving from P, from $\theta$ to $(\theta+\alpha)$.

Fig. 2.




The velocity parallel to Oz acquired in the field over the path PO is $\frac{Ze}{m} \cdot \frac{r}{U}$, terms in $Z^2$ being neglected, so that the angle $\alpha$ is given by

$$\sin \alpha = \frac{Zer}{mU^2} \sin \theta.$$

The projection of $d$S normal to the beam PO is therefore changed to $\cos(\theta+\alpha)$, and the number of electrons

which collide within $d\tau$ per second and traverse $d\mathrm{S}$ without further collision is

$$\frac{n\mathrm{U}}{l}\, e^{-r/l}\frac{d\mathrm{S}\cos(\theta+\gamma)}{4\pi r^2}\,d\tau.$$

If the angle $\alpha$ is small, then in the expansion of $\cos(\theta+\alpha)$, $\cos\alpha$ may be put equal to unity.

The total number of electrons projected downwards across $d\mathrm{S}$ per second from the whole space above the plane $x\mathrm{O}y$ is

$$\nu_- = \sum\frac{n\mathrm{U}}{l}\, e^{-r/l}\frac{d\mathrm{S}\cos(\theta+\alpha)}{4\pi r^2}\,d\tau$$

$$= \frac{\mathrm{U}}{l}\frac{d\mathrm{S}}{4\pi}\int_0^{2\pi}\int_0^{\pi/2}\int_0^{\infty}\left(n_0+r\cos\theta\,.\,\frac{dn}{dz}\right)e^{-r/l}\sin\theta$$

$$\cdot\left(\cos\theta-\frac{Zer}{m\mathrm{U}^2}\sin^2\theta\right)d\phi\,d\theta\,dr$$

$$= \frac{d\mathrm{S}}{2}\left[\frac{n_0\mathrm{U}}{2}+\left(\frac{1}{3}l\mathrm{U}-\frac{Zel^2}{4m\mathrm{U}^2}\right)\frac{dn}{dz}-n_0\,.\,\frac{2}{3}\frac{Zel}{m\mathrm{U}}\right].$$

Put

$$\frac{1}{3}l\mathrm{U}=\mathrm{K}_v \quad\text{and}\quad \frac{2}{3}\frac{Zel}{m\mathrm{U}}=\mathrm{W}_v,$$

then

$$\nu_- = \frac{d\mathrm{S}}{2}\left[\frac{n_0\mathrm{U}}{2}+\mathrm{K}_v\left(1-\frac{9}{8}\frac{\mathrm{W}_v}{\mathrm{U}}\right)\frac{dn}{dx}-n_0\mathrm{W}_v\right]. \quad . \quad (2)$$

The number of electrons crossing $d\mathrm{S}$ per second in the reverse direction is, similarly,

$$\nu_+ = \frac{d\mathrm{S}}{2}\left[\frac{n_0\mathrm{U}}{2}-\mathrm{K}_v\left(1-\frac{9}{8}\frac{\mathrm{W}_v}{\mathrm{U}}\right)\frac{dn}{dz}+n_0\mathrm{W}_v\right].$$

The net transport $(\nu_+-\nu_-)$ in the direction $\mathrm{O}z$ is

$$(\nu_+-\nu_-) = \left[-\mathrm{K}_v\left(1-\frac{9}{8}\frac{\mathrm{W}_v}{\mathrm{U}}\right)\frac{dn}{dz}+n_0\mathrm{W}\right]d\mathrm{S}.$$

In many experiments the velocity W is at the most a few per cent. of the velocity U, so that the term $\frac{\mathrm{W}_v}{\mathrm{U}}$ may be omitted.

In these circumstances the curvature of the free paths, as represented by $\left(1-\frac{9}{8}\frac{W_U}{U}\right)$, is slight in the field Z, and the field affects the process of diffusion only through the velocity U.

When a distribution of the velocities U about a mean value is admitted, the net transport of electrons per second across $d$S in the direction Oz may be written

$$\dot{n}_0 w = -K\frac{dn}{dz} + n_0 W, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\left.\begin{aligned} K &= (\overline{K_U}) = \frac{1}{3}(\bar{l}\bar{U}), \\ W &= (\overline{W_U}) = \frac{2}{3}\frac{Ze}{m}\left(\frac{\bar{l}}{\bar{U}}\right). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

This definition of the mean velocity of transport $w$ is the same as that used in Maxwell's equations for the [4] inter-diffusion of gases.

The total transport velocity $w$ may, in these circumstances, be obtained by superposition of the velocities of drift in the field and of diffusion, which exist in the steady state appropriate to the field Z.

The partial pressure of the electrons (suppressing the subscript to $n$) is

$$p = \tfrac{1}{3} nm\bar{U}^2,$$

so that equation (3) may be written

$$\frac{pw}{K} = -\frac{dp}{dz} + \frac{pW}{K} \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

When the force Z is absent this reduces to $\frac{pw}{K} = -\frac{dp}{dz}$, in which $p$, in general assumes a different value from that in (3) with Z operating.

The term on the right is the momentum parallel to Oz communicated to unit volume per second by the transport of electrons over its bounding surfaces. Consequently, the term on the left gives the momentum lost in collisions with molecules per unit volume per second under the steady velocity $w$.

When the field Z is applied and the ratio W/U is small, the momentum communicated to unit volume per second

increases to $-\frac{dp}{dz}+neZ$, where $-\frac{dp}{dz}$ is the steady pressure gradient which prevails with the applied force $neZ$, while that lost per second is again $\frac{pw}{K}$, where $w$ is given by (3 $a$).

Maxwell's equations of interdiffusion [4], [5] result immediately and correspond to the case in which one of the gases is present in small proportion.

$$\frac{pu}{K}=-\frac{\partial p}{\partial x}+neX,$$

$$\frac{pv}{K}=-\frac{\partial p}{\partial y}+neY,$$

$$\frac{pw}{K}=-\frac{\partial p}{\partial z}+neZ.$$

Comparison with (3 $a$) gives the well-known relation [5]

$$\frac{W}{K}=\frac{neZ}{p}. \quad \ldots\ldots\ldots \quad (6)$$

On substituting in equation (6) for W and K, the values (4), and for $p=\frac{1}{3}nm\overline{U^2}$, the following relation is obtained,

$$\frac{2}{3}\left(\frac{\overline{l}}{U}\right)=\frac{\overline{lU}}{\overline{U^2}}, \quad \ldots\ldots\ldots \quad (7)$$

so that the distribution function for the velocities U possesses the above property.

When $l$ is independent of U, (7) reduces to $\frac{2}{3}\left(\frac{\overline{l}}{U}\right)=\frac{\overline{U}}{\overline{U^2}}$ which is a property of Maxwell's distribution function, so that the latter is a possible distribution [1] function for electrons moving through a gas in a steady motion under an electric field. In this particular instance the formula for W reduces to

$$W=\frac{2}{3}\frac{Ze}{m}\left(\frac{\overline{l}}{U}\right)=\frac{\overline{U}}{\sqrt{\overline{U^2}}}\cdot\frac{Zel}{m\sqrt{\overline{U^2}}}=\cdot 92\,\frac{Zel}{m\sqrt{\overline{U^2}}},$$

a useful form involving the experimental quantity $\overline{U^2}$.

The distributions of the velocities U about their mean values have been discussed by Pidduck [6], Druyvesteyn [7], Townsend [1], [8], Morse and others [9], and Jones [10], and it is unnecessary to mention the subject further here.

### III. *Diffusion of Electrons in a Magnetic Field.*

Townsend [2] has shown that, whereas the coefficient of diffusion $K_U$ in the direction of the magnetic field H is unaffected by the field, in directions normal to H the coefficient is reduced to $(K_h)_U$, where

$$(K_h)_U = \frac{K_U}{1+\omega^2 T^2} = \frac{1}{3} \cdot \frac{lU}{(1+\omega^2 T^2)},$$

in which $\omega = \frac{He}{m}$, $T = \frac{l}{U}$, and all the electrons are supposed to move with the common velocity of agitation U. With a distribution of velocities the formula becomes

$$K_h = (\overline{K_h})_U = \frac{1}{3}\left(\overline{\frac{lU}{1+\omega^2 T^2}}\right).$$

This formula may also be obtained by a geometrical method.

Let the magnetic field H be directed along O$z$, fig. 3, and consider an electron which leaves the origin O with velocity U making an angle $\theta$ with O$z$, and whose projection U $\sin\theta$ on the plane $x$O$y$ makes an initial angle $\beta$ with O$x$.

The electron describes a helical orbit in the field H, on the surface of a cylinder whose axis is parallel to O$z$ whose radius $a$ is $\frac{mU\sin\theta}{He} = \frac{U\sin\theta}{\omega}$, and which intersects the plane $x$O$z$ along O$z$ at an angle $\beta$.

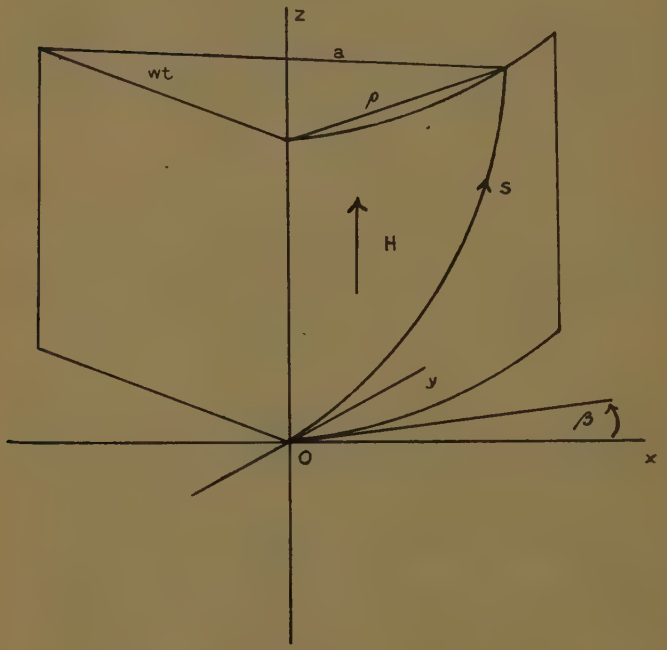
The angular velocity in the plane $x$O$y$ of the radius $a$ which gives the distance of the electron from the axis of the cylinder is $\omega$, so that when the electron has travelled a distance $s$ in time $t = \frac{s}{U}$ its distance $\rho$ from the axis O$z$ is given by

$$\rho = 2a \sin\frac{\omega t}{2} = \frac{2U\sin\theta}{\omega} \sin\frac{\omega s}{2U}.$$

As all initial directions $\beta$ are equally probable, the mean value of $\rho^2$ for given values of $s$ and U is

$$\overline{\rho^2} = \frac{4U^2}{\omega^2} \sin^2 \frac{\omega s}{2U} \cdot \frac{1}{2} \int_0^{\pi} \sin^3 \theta \, d\theta = \frac{8}{3} \frac{U^2}{\omega^2} \cdot \sin^2 \frac{\omega s}{2U}.$$

Fig. 3.




The mean value of $\rho^2$ for those free paths traversed at velocity U, but whose lengths $s$ may have any value, is

$$\overline{\overline{\rho^2}} = \frac{8}{3} \frac{U^2}{\omega^2} \int_0^{\infty} \frac{e^{-s/l}}{l} \sin^2 \frac{\omega s}{2U} \, ds = \frac{8}{3} \frac{U^2}{\omega^2} \int_0^{\infty} e^{-\tau/T} \sin^2 \frac{\omega \tau}{2} \cdot d\tau$$

$$= \frac{4}{3} \cdot \frac{l^2}{(1+\omega^2 T^2)} = \overline{\overline{\Delta x^2}} + \overline{\overline{\Delta y^2}},$$

where $\tau = s/U$ and $T = l/U$.

Consequently,

$$\overline{\overline{\Delta x^2}} = \frac{2}{3} \frac{l^2}{(1+\omega^2 \tau^2)}.$$

In a large group $n$ of electrons, let $n_u$ be the number at any instant whose velocities have the value U.

The number of collisions made by such electrons in one second is $n_u \frac{U}{P} = \frac{n_u}{T}$, so that the aggregate of the squares of the increments in the $x$ coordinates due to these collisions is

$$\frac{n_u}{T}\overline{\Delta x^2} = \frac{2}{3}\frac{lU.n_u}{(1+\omega^2\Gamma^2)}.$$

On averaging over all velocities U and using the well-known result $\frac{d}{dt}(x^2)=2K$, the formula for $K_h$ given above is obtained :

$$K_h = \frac{1}{3}\left(\frac{\overline{lU}}{1+\omega^2T^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

IV. *Motion with combined Electric and Magnetic Fields.*

The formula which has been derived [2] and used [2], [3] for the velocity $W_x$ in the direction of the electric force X when the field H acts along Oz is $\frac{Xe}{m} \cdot \frac{T}{(1+\omega^2T^2)}$, where all velocities U are taken to be equal and $\omega$ and T have the meanings assigned in the previous section.

When H=0, this reduces to $\frac{Xe}{m} \cdot \frac{l}{U}$ and is the same as expression (1) with the coefficient $g$ unity instead of 2/3; consequently, the formula is inexact.

Although the formulæ for the velocities $W_x$ and $W_y$ along the axes Ox and Oy are incorrect, the important formula for the deflexion of a stream of electrons by a transverse magnetic field, namely, $\tan\theta = \frac{HW}{X}$, on which are based measurements of the velocity of drift W from the deflexion $\theta$, requires inessential modifications.

Consequently, the many important conclusions which are based upon the values of the velocities W measured [11], [12] in this way are in no way affected.

Choose a coordinate system in which the axis Ox coincides with the direction of the magnetic field H.

Let the components of the electric field in this system be X, Y, and Z.

The equations of motion are, $e$ being considered positive,

$$\left.\begin{aligned} m\ddot{x} &= \mathrm{X}e + \mathrm{H}e\dot{y}, \\ m\ddot{y} &= \mathrm{Y}e - \mathrm{H}e\dot{x}, \\ m\ddot{z} &= \mathrm{Z}e, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (9)$$

the forces H, X, Y, and Z, and the charge $e$ being in electromagnetic units.

Let the electron start at the origin at time $t=0$, with a velocity U whose components are $v_x$, $v_y$, and $v_z$, so that the initial conditions are

$$\left.\begin{aligned} &\text{at } t=0, \qquad x=y=z=0, \\ &\qquad\qquad \dot{x}=v_x\,; \quad \dot{y}=v_y\,; \quad \dot{z}=v_z. \end{aligned}\right\} \quad . \quad . \quad . \quad (10)$$

The solutions of (9) for the velocities and displacements which satisfy the initial conditions are :

$$\left.\begin{aligned} \dot{x} &= \frac{\mathrm{Y}}{\mathrm{H}} + \mathrm{C}\sin(\omega t+\alpha), \\ \dot{y} &= -\frac{\mathrm{X}}{\mathrm{H}} + \mathrm{C}\cos(\omega t+\alpha), \\ \dot{z} &= \frac{\mathrm{Z}e}{m}t + v_z, \end{aligned}\right\} \quad . \quad . \quad . \quad (11)$$

and

$$\left.\begin{aligned} x &= \frac{\mathrm{Y}t}{\mathrm{H}} + \frac{\mathrm{C}}{\omega}[\cos\alpha - \cos(\omega t+\alpha)], \\ y &= -\frac{\mathrm{X}t}{\mathrm{H}} + \frac{\mathrm{C}}{\omega}[\sin(\omega t+\alpha) - \sin\alpha], \\ z &= v_z t + \frac{1}{2}\frac{\mathrm{Z}e}{m}t^2, \end{aligned}\right\} \quad . \quad . \quad (12)$$

in which

$$\left.\begin{aligned} \mathrm{C}\cos\alpha &= \left(v_y + \frac{\mathrm{X}}{\mathrm{H}}\right), \\ \mathrm{C}\sin\alpha &= \left(v_z - \frac{\mathrm{Y}}{\mathrm{H}}\right), \\ \mathrm{C}^2 &= \left(v_y + \frac{\mathrm{X}}{\mathrm{H}}\right)^2 + \left(v_z - \frac{\mathrm{Y}}{\mathrm{H}}\right)^2. \end{aligned}\right\} \quad . \quad . \quad (13)$$

At time $t$ the square of the orbital velocity, $\frac{ds}{dt}$, is

$$\left(\frac{ds}{dt}\right)^2 = \dot{x}^2+\dot{y}^2+\dot{z}^2$$

$$= \frac{Y^2}{H^2}+2\frac{Y}{H}C\sin(\omega t+\alpha)+C^2\sin^2(\omega t+\alpha)$$

$$+\frac{X^2}{H^2}-2\frac{X}{H}C\cos(\omega t+\alpha)+C^2\cos^2(\omega t+\alpha)$$

$$+v_x^2+2v_x\frac{Ze}{m}.t+\left(\frac{Ze}{m}\right)^2t^2.$$

When $U^2$ is written for $(v_x^2+v_y^2+v_z^2)$ and relations (13) are used, this reduces to

$$\left(\frac{ds}{dt}\right)^2 = 2\left(\frac{X^2+Y^2}{H^2}\right)(1-\cos\omega t)$$

$$+\frac{2X}{H}[v_y(1-\cos\omega t)+v_z\sin\omega t]$$

$$-\frac{2Y}{H}[v_x(1-\cos\omega t)-v_y\sin\omega t]$$

$$+\frac{2Ze}{m}.v_zt+\frac{Z^2e^2}{m^2}t^2+U^2. \quad . \quad . \quad . \quad . \quad (14)$$

It will be supposed, as generally obtains in practice, that the velocities acquired along a free path $s$, due to the action of the electric field, are small compared with the velocity of agitation U, so that the terms in equation (14) involving X, Y, and Z are small compared with $U^2$, and those in the squares of the components of the electric force, negligible.

With this limitation on the magnitude of the electric force, equation (14) can be simplified to

$$\frac{ds}{dt} = U\left[1+\frac{2}{U^2H}\{X[v_y(1-\cos\omega t)+v_x\sin\omega t]\right.$$

$$\left.-Y[v_x(1-\cos\omega t)-v_y\sin\omega t]\}+\frac{2Ze}{U^2m}.v_zt\right]^{1/2}$$

$$\doteq U+\frac{1}{UH}\{X[v_y(1-\cos\omega t)+v_x\sin\omega t]$$

$$-Y[v_x(1-\cos\omega t)-v_y\sin\omega t]\}+\frac{Ze}{mU}.v_zt.$$

Thus, to a first approximation the orbital distance $s$ travelled in time $t$ is

$$s = \mathrm{U}t + \frac{1}{\mathrm{UH}}\left\{\left(t - \frac{\sin\omega t}{\omega}\right)(\mathrm{X}v_y - \mathrm{Y}v_x) + (\mathrm{X}v_x + \mathrm{Y}v_y)\left(\frac{1-\cos\omega t}{\omega}\right)\right\} + \frac{\mathrm{Z}e}{2m}\cdot\frac{v_z}{\mathrm{U}}t^2. \quad (15)$$

The predominating term on the right is $\mathrm{U}t$ and to a first approximation the time $t'$ to describe a free path [1] $s$ is

$$t' = \frac{s}{\mathrm{U}} - \Delta,$$

where

$$\Delta = \frac{1}{\omega\mathrm{HU}^2}\left\{(\mathrm{X}v_y - \mathrm{Y}v_x)\left(\frac{\omega s}{\mathrm{U}} - \sin\frac{\omega s}{\mathrm{U}}\right) + (\mathrm{X}v_x + \mathrm{Y}v_y)\left(1-\cos\frac{\omega s}{\mathrm{U}}\right)\right\} + \frac{\mathrm{Z}ev_z}{2m}\cdot\frac{s^2}{\mathrm{U}^4}. \quad (16)$$

The displacement $x_{t'}$ in the time $t'$ required to describe the free path $s$ is

$$\begin{aligned} x_{t'} &= \frac{\mathrm{Y}t'}{\mathrm{H}} + \frac{\mathrm{C}}{\omega}[\cos\alpha - \cos(\omega t' + \alpha)] \\ &= x_{s/\mathrm{U}} - \Delta\left(\frac{dx}{dt}\right)_{s/\mathrm{U}} \\ &= \frac{\mathrm{Y}s}{\mathrm{UH}} + \frac{\mathrm{C}}{\omega}\left[\cos\alpha - \cos\left(\frac{\omega s}{\mathrm{U}} + \alpha\right)\right] \\ &\qquad - \Delta\left[\frac{\mathrm{C}}{\omega}\,\omega\sin\left(\frac{\omega s}{\mathrm{U}} + \alpha\right) + \frac{\mathrm{Y}}{\mathrm{H}}\right], \end{aligned}$$

which when expanded becomes

$$\begin{aligned} x_{t'} = {} & \frac{\mathrm{Y}}{\mathrm{H}}\cdot\frac{s}{\mathrm{U}} + \frac{1}{\omega}\left[\left(v_y + \frac{\mathrm{X}}{\mathrm{H}}\right)\left(1-\cos\frac{\omega s}{\mathrm{U}}\right) + \left(v_x - \frac{\mathrm{Y}}{\mathrm{H}}\right)\sin\frac{\omega s}{\mathrm{U}}\right] \\ & - \left\{\frac{1}{\omega\mathrm{HU}^2}\left[(\mathrm{X}v_y - \mathrm{Y}v_x)\left(\frac{\omega s}{\mathrm{U}} - \sin\frac{\omega s}{\mathrm{U}}\right)\right.\right. \\ & \left.\left. + (\mathrm{X}v_x + \mathrm{Y}v_y)\left(1-\cos\frac{\omega s}{\mathrm{U}}\right)\right] + \frac{\mathrm{Z}ev_z}{2m}\cdot\frac{s^2}{\mathrm{U}^3}\right\} \\ & \times\left\{\left(v_y + \frac{\mathrm{X}}{\mathrm{H}}\right)\sin\frac{\omega s}{\mathrm{U}} + \left(v_x - \frac{\mathrm{Y}}{\mathrm{H}}\right)\cos\frac{\omega s}{\mathrm{U}} + \frac{\mathrm{Y}}{\mathrm{H}}\right\}. \quad (17) \end{aligned}$$

To obtain the average displacement $\bar{x}_{t'}$ for all values of $v_x$, $v_y$, and $v_z$, with $s$ and U constant, expand the above expression, put $\overline{v_x^2}=\overline{v_y^2}=\overline{v_z^2}$ equal to $U^2/3$, and reject terms involving the forces to the second degree, and those in $\overline{v_x}$, $\overline{v_y}$, $\overline{v_z}$, $\overline{v_xv_y}$, $\overline{v_yv_z}$, and $\overline{v_yv_z}$ which vanish in the mean. We find,

$$\begin{aligned}\bar{x}_{t'} &= \frac{Y}{H}\frac{s}{U}+\frac{1}{\omega}\frac{X}{H}\left(1-\cos\frac{\omega s}{U}\right)-\frac{1}{\omega}\frac{X}{H}\sin\frac{\omega s}{U}\\
&\quad-\frac{1}{\omega H}\left\{\frac{1}{3}\left(\sin\frac{\omega s}{U}\right)\left[X\left(\frac{\omega s}{U}-\sin\frac{\omega s}{U}\right)+Y\left(1-\cos\frac{\omega s}{U}\right)\right]\right.\\
&\quad\left.-\frac{1}{3}\left(\cos\frac{\omega s}{U}\right)\left[Y\left(\frac{\omega s}{U}-\sin\frac{\omega s}{U}\right)-X\left(1-\cos\frac{\omega s}{U}\right)\right]\right\}\\
&=\frac{4}{3}\frac{X}{H\omega}\left(1-\cos\frac{\omega s}{U}\right)-\frac{X}{3\omega H}\cdot\frac{\omega s}{U}\sin\frac{\omega s}{U}\\
&\quad+\frac{Ys}{U}-\frac{4}{3}\frac{Y}{\omega H}\sin\frac{\omega s}{U}+\frac{1}{3}\frac{Y}{H\omega}\cdot\frac{\omega s}{U}\cos\frac{\omega s}{U}\quad\ldots\quad(18)\end{aligned}$$

We next obtain the mean displacement $\bar{\bar{x}}$ corresponding to a given velocity U by averaging the quantity $x_{t'}$ over all values of the mean free path $s$; that is, by evaluating the expression

$$\bar{\bar{x}}=\frac{1}{T}\int_0^\infty \bar{x}e^{-\tau/T}\,d\tau,$$

where $\tau=s/U$, $T=l/U$, and $\bar{x}$ is the expression on the right-hand side of (18).

The necessary integrals are given in an appendix.

It will be found that

$$\begin{aligned}\bar{\bar{x}}&=\frac{4X}{3\omega H}\cdot\frac{\omega^2T^2}{(1+\omega^2T^2)}-\frac{X}{3\omega H}\cdot\frac{2\omega^2T^2}{(1+\omega^2T^2)}\left[1-\frac{\omega^2T^2}{1+\omega^2T^2}\right]\\
&\quad+\frac{YT}{H}-\frac{4Y}{3\omega H}\cdot\frac{\omega T}{(1+\omega^2T^2)}\\
&\quad+\frac{Y}{3H}\cdot\frac{T}{(1+\omega^2T^2)}\left[1-\frac{2\omega^2T^2}{(1+\omega^2T^2)}\right]\\
&=\frac{2X}{3H}\cdot\frac{\omega T^2}{(1+\omega^2T^2)}\left[1+\frac{\omega^2T^2}{1+\omega^2T^2}\right]\\
&\quad+\frac{YT}{H}\cdot\frac{\omega^2T^2}{(1+\omega^2T^2)^2}\left[\tfrac{1}{3}+\omega^2T^2\right].\quad(19)\end{aligned}$$

Consider a group of a large number $n$ of electrons, and let $n_u$ be those which at any instant possess the velocity U.

The number of collisions per second which terminate free paths for which the initial velocity is U is $\frac{n_u U}{\bar{l}} = \frac{n_u}{\bar{T}}$, and for each of these the mean displacement is $\bar{x}$, so that the mean velocity of drift $(W_x)_u$ appropriate to the class $n_u$ is

$$(W_x)_U = \frac{2}{3}\frac{X}{H}\cdot\frac{\omega T}{(1+\omega^2T^2)}\left[1+\frac{\omega^2T^2}{1+\omega^2T^2}\right] + \frac{Y}{H}\cdot\frac{\omega^2T^2}{(1+\omega^2T^2)^2}\left[\tfrac{1}{3}+\omega^2T^2\right], \quad (20)$$

and the mean velocity of drift $W_x$ of the whole group of $n$ electrons becomes

$$W_x = (\overline{W_x})_U = \frac{2}{3}\frac{X}{H}\cdot\overline{\frac{\omega T}{(1+\omega^2T^2)}\left[1+\frac{\omega^2T^2}{1+\omega^2T^2}\right]} + \frac{Y}{H}\cdot\overline{\frac{\omega^2T^2}{(1+\omega^2T^2)^2}\left[\tfrac{1}{3}+\omega^2T^2\right]}. \quad (21)$$

In this expression X is restricted to small values such that $W_x/U$ is also small, but no limitation has been postulated for $\omega T$. In many laboratory experiments $\omega T$ is small and the free paths are small compared with their radii of curvature. In these circumstances the expression (21) may be simplified by considering the terms in the square brackets as unity and $\frac{1}{3}$ respectively.

The term in Y also becomes small compared with that in X.

Put $Y=0$, and let H vanish, and $\omega$ therefore with it.

$W_x$ becomes

$$\frac{2}{3}\frac{X}{H}\overline{\omega T} = \frac{2}{3}\frac{Xe}{m}\left(\frac{\bar{l}}{\bar{U}}\right)$$

in agreement with (1) when $g$ has its correct value.

The expression for the velocity W in the direction $Oy$ is, similarly,

$$W_y = \frac{2}{3}\frac{Y}{H}\overline{\frac{\omega T}{(1+\omega^2T^2)}\left[1+\frac{\omega^2T^2}{1+\omega^2T^2}\right]} - \frac{X}{H}\cdot\overline{\frac{\omega^2T^2}{(1+\omega^2T^2)^2}\left(\tfrac{1}{3}+\omega^2T^2\right)}. \quad (22)$$

The velocity $W_z$ along Oz is found as follows :—

According to equation (12), the displacement $z_{t'}$ in the direction Oz in time $t'=s/U-\Delta$ is

$$z_{t'}=v_z\frac{s}{U}-v_z\Delta+\frac{1}{2}\frac{Ze}{m}\frac{s^2}{U^2}-\frac{Ze}{m}\frac{s}{U}\Delta+\Delta^2.$$

Average as before, and discard terms of the second degree in the forces to obtain

$$\overline{z_{t'}}=-\frac{Ze}{2m}\frac{\overline{s^2}}{U^2}\frac{1}{3}+\frac{1}{2}\frac{Ze}{m}\frac{\overline{s^2}}{U}$$

$$=\frac{1}{3}\frac{Ze\overline{s^2}}{mU^2}.$$

The mean of $s^2$ is $2l^2$, so that

$$\bar{z}=\frac{2}{3}\frac{Ze}{m}\cdot\frac{\overline{l^2}}{U^2}$$

and the velocity $(W_z)_u=\frac{2}{3}\frac{Ze}{m}\left(\frac{\bar{l}}{U}\right)$.

Finally, the velocity $W_z=\frac{2}{3}\frac{Ze}{m}\left(\frac{\bar{l}}{U}\right)$, and is independent of the magnetic field.

## V. *Deflexion of a Stream of Electrons by a Transverse Magnetic Field.*

Put Y=Z=0, then

$$\left.\begin{aligned}W_x&=\frac{2}{3}\frac{X}{H}\overline{\frac{\omega T}{1+\omega^2T^2}\left[1+\frac{\omega^2T^2}{1+\omega^2T^2}\right]},\\ W_y&=-\frac{X}{H}\overline{\frac{\omega^2T^2}{(1+\omega^2T^2)}\left[\tfrac{1}{3}+\omega^2T^2\right]},\\ W_z&=0.\end{aligned}\right\}\quad\ldots\quad(23)$$

The expression for the velocity $W_y$ is, however, in an inconvenient form, as it requires for its transformation a knowledge of the properties of the distribution function for the quantities T about their mean. An alternative expression will therefore be deduced.

When Y, Z, and Grad $p$ are zero the diffusion equations reduce to

$$\frac{p\mathrm{W}_x}{\mathrm{K}_x} = ne\mathrm{X} + \overset{n}{\Sigma}\mathrm{H}e\dot{y},$$

$$\frac{p\mathrm{W}_y}{\mathrm{K}_y} = -\overset{n}{\Sigma}\mathrm{H}e\dot{x},$$

where $n$ is the number of electrons per unit volume, $k_x = k_y = k_h = \frac{1}{3}\left(\frac{l\mathrm{U}}{1+\omega^2\mathrm{T}^2}\right)$, as given by (8), $\overset{n}{\Sigma}\mathrm{H}e\dot{x}$ the momentum parallel to. O$y$ communicated per second to unit volume by the reaction of the magnetic field and the $n$ moving charges, and $\overset{n}{\Sigma}\mathrm{H}e\dot{y}$ the similar quantity relative to the axis O$x$.

The terms $\overset{n}{\Sigma}\mathrm{H}e\dot{x}$ and $\overset{n}{\Sigma}\mathrm{H}e\dot{y}$ may be simply evaluated as follows :

The momentum communicated in the direction O$y$ to an electron, as it traverses a free path $s$ in time $t' = s/\mathrm{U} - \Delta$, is

$$\int_0^{t'} \mathrm{H}e\dot{x}\,dt = \mathrm{H}ex_{t'},$$

where $x_{t'}$ is the displacement of the electron in the direction O$x$ during a free path $s$, and is given by equation (17).

It follows that, in averaging this quantity over all free paths and velocities U, the value finally found for the momentum $\overset{n}{\Sigma}\mathrm{H}e\dot{x}$ communicated to the $n$ electrons in unit volume, per second, is the sum of their displacements $x_{t'}$ in unit time multiplied by H$e$, giving $n\mathrm{H}e\mathrm{W}_x$. In the same way $\overset{n}{\Sigma}\mathrm{H}e\dot{y}$ becomes $n\mathrm{H}e\mathrm{W}_y$.

Consequently, when Y$=0$,

$$\left.\begin{aligned} \frac{p\mathrm{W}_x}{\mathrm{K}_x} &= ne\mathrm{X} + ne\mathrm{H}\mathrm{W}_y, \\ \frac{p\mathrm{W}_y}{\mathrm{K}_y} &= -ne\mathrm{H}\mathrm{W}_x, \\ \mathrm{K}_x &= \mathrm{K}_y = \mathrm{K}_h. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (24)$$

The lateral deflexion $\theta$ from the direction $Ox$ resulting from the application of the field H along $Oz$ is such that

$$\tan\theta = \frac{W_y}{W_x},$$

whence it follows, from division of the first of equations (24) by the second, that

$$\sin 2\theta = -\frac{2H}{X} W_x$$

$$\text{or} \qquad W_x = -\frac{1}{2}\frac{X}{H}\sin 2\theta. \quad . \quad . \quad . \quad . \quad (25)$$

This formula differs from that used hitherto for the deflexion, in the substitution of $W_x$ for W, the velocity when H is zero, and of $\frac{1}{2}\sin 2\theta$ for $\tan\theta$.

In many experimental determinations of velocities W from the deflexion $\theta$, both in gases [11], [12] and in flames [13], $\theta$ is a small angle, so that $\omega T$ is small compared with unity [2]. In this case the formula reduces to $W = -\frac{X}{H}\theta$, $W_x$ being sensibly identical with W, as the term $neHW_y$ in (24) becomes negligible in comparison with $neX$.

The formula then coincides with that in $\tan\theta$ used previously, and it is unnecessary to introduce corrections to the published values of the velocities W.

When $\omega T$ is small, it follows also that an alternative expression for $W_y$ is

$$W_y = -neH \cdot \frac{K_h}{p} W_x = -\frac{neH}{neX} W_x^2$$

$$= -\frac{H}{X} W_x^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This reduces to

$$W_y = -\frac{4}{9}\frac{X}{H}\left[\left(\frac{\omega T}{1+\omega^2 T^2}\right)\left(1+\frac{\omega^2 T^2}{1+\omega^2 T^2}\right)\right]^2$$

$$\doteqdot -\frac{4}{9}\frac{X}{H}\left(\frac{\omega T}{1+\omega^2 T^2}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26a)$$

We thus obtain a transformation formula, when $\omega T$ is small, for the average of the quantity appearing in equation (23).

In general, as for instance in the ionosphere [3], $\omega T$ is not small compared with unity, and relation (26) is incorrect.

The following equation for $W_y$ is obtained from (24):

$$W_y^2 + \frac{X}{H} W_y + W_x^2 = 0,$$

so that

$$2W_y = -\frac{X}{H} \pm \sqrt{\frac{X^2}{H^2} - 4W_x^2},$$

where $W_x$ has the value given in (23).

$W_y$ vanishes with H, so that on taking the positive sign before the radical we find when H is small

$$2W_y \doteqdot -\frac{X}{H} + \frac{X}{H}\left(1 - \frac{2H^2}{X^2} W_x^2 + \ldots\right)$$

$$\doteqdot -\frac{2HW_x^2}{X},$$

which agrees with (26).

When, however, $\omega T$ becomes large, $W_x \to 0$, so that, adopting the negative sign before the radical,

$$2W_y = -\frac{X}{H} - \frac{X}{H}\left(1 - \frac{2H^2}{X^2} W_x^2 + \ldots\right)$$

$$= -\frac{2X}{H} + \frac{2H}{X} W_x^2 - \ldots$$

For $T \to \infty$, we find, therefore, $W_x \to 0$, $W_y \to -\frac{X}{H}$ in agreement with equations (11) for the free orbit.

Formulæ (23) are also consistent with these conclusions.

Finally, the general form of the equations of diffusion, when H acts along Oz, is

$$\left.\begin{aligned} \frac{pu}{K_x} &= -\frac{\partial p}{\partial x} + neX + neHW_y, \\ \frac{pv}{K_y} &= -\frac{\partial p}{\partial y} + neY - neHW_x, \\ \frac{pw}{K} &= -\frac{\partial p}{\partial z} + neZ. \end{aligned}\right\} \quad \ldots \quad (27)$$

The directions of the forces and velocities are correctly obtained for electrons, by putting the charge negative in the various equations which have preceded.

## VI. *Appendix.*

$$\int_0^\infty e^{-\tau/T} \cos \omega\tau \, d\tau = \frac{T}{1+\omega^2T^2},$$

$$\int_0^\infty e^{-\tau/T} (1-\cos \omega\tau) \, d\tau = \frac{\omega^2T^3}{(1+\omega^2T^2)},$$

$$\int_0^\infty e^{-\tau/T} \sin \omega\tau \, d\tau = \frac{\omega T^2}{1+\omega^2T^2},$$

$$\int_0^\infty e^{-\tau/T} \tau \cos \omega\tau \, d\tau = \frac{T^2}{(1+\omega^2T^2)}\left[1-\frac{2\omega^2T^2}{1+\omega^2T^2}\right],$$

$$\int_0^\infty e^{-\tau/T} \tau \sin \omega\tau \, d\tau = \frac{2\omega T^3}{(1+\omega^2T^2)^2}\left[1-\frac{\omega^2T^2}{1+\omega^2T^2}\right],$$

$$\int_0^\infty e^{-\tau/T} \sin^2 \frac{\omega\tau}{2} d\tau = \frac{1}{2}\frac{\omega^2T^3}{(1+\omega^2T^2)}.$$

*Summary.*

The correct formula for the velocity of drift W of a group of electrons through a gas in the counter-direction to the electric field X is $g \cdot \frac{Xe}{m} \cdot \left(\frac{l}{U}\right)$, in which the coefficient $g=2/3$. Townsend has recently given two proofs of this formula and has indicated a fallacy in some previous deductions. The existing formulæ for the velocities $W_x$ and $W_y$ in the direction of X and transverse to it when a magnetic field is present are inexact for the same reason, and as they are of wide application their correct form is derived in this paper. In the particular instance in which the electric force X acts along O$x$ and the magnetic field H along O$z$ the revised formula for $W_x$ is

$$\frac{2}{3}\frac{X}{H} \cdot \frac{\omega T}{(1+\omega^2T^2)}\left(1+\frac{\omega^2T^2}{1+\omega^2T^2}\right),$$

where $\omega = \frac{He}{m}$ and $T = \frac{l}{U}$, $l$ being the mean free path appropriate to the velocity of agitation U of the electron.

The lateral deviation $\theta$ of an electronic stream by a transverse magnetic field is given by $\frac{1}{2}\sin 2\theta = -\frac{HW_x}{X}$, and when $\theta$ is a small angle this formula coincides with that previously used $\left(\text{viz., } \tan\theta = -\frac{HW}{X}\right)$ in the measurement of the velocities W. It is therefore unnecessary to correct the published values for the velocities W measured by the method of magnetic deflexion.

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(1) Townsend, J. S., Phil. Mag. xxii. p. 145 (1936).
(2) Townsend, J. S., Proc. Roy. Soc. A, lxxxvi. p. 571 (1912); 'Electricity in Gases,' pp. 96 and 100.
(3) Appleton, E. V., Phys. Soc. Report on Progress in Physics, ii. p. 162 (1935); Bailey, V. A., and Martyn, D. F., Phil. Mag. xviii. p. 369 (1934).
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(8) Townsend, J. S., Phil. Mag. ix. p. 1145 (1930).
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(11) Townsend, J. S. 'Electricity in Gases,' §§ 104 and 105, chap. v. "Motion of Electrons in Gases," (Oxford).
(12) Bailey, V. A., Phil. Mag. ix. p. 560 (1930); *Ibid.*, p. 625.
(13) Wilson, H. A., 'Modern Physics,' p. 257 (Blackie).

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## XXI. *On the Loss of Energy by α-particles in Hydrogen.* *By* Prof. K. C. Kar, *D.Sc.*, *and* K. K. Mukherjee, *M.Sc.**

IT is well known that the velocity of the α-particles emitted by radioactive substances is determined from an experimental measurement of the range and the empirical relation of Geiger-Nuttall, connecting the range with the velocity. An attempt to deduce a similar formula on theoretical grounds was made by Bohr† as early as 1913. Recently Gaunt‡ and Bethe§ have

* Communicated by the Authors.
† Bohr, Phil. Mag. xxv. p. 10 (1913).
‡ Gaunt, Proc. Camb. Phil. Soc. xxiii. p. 732 (1925–27).
§ Bethe, *Ann. der Phys.* v. p. 325 (1930); see also Bethe-Heitler, Proc. Roy. Soc. cxlvi. p. 83 (1934).

deduced the corresponding wave-mechanical formulæ. In these theories the classical dynamics is freely used at a later stage, to arrive at a formula somewhat analogous to that of Bohr. It may be noted that Bethe's formula involves a function which is computed with difficulty *.

In developing the wave-statistical theory of the problem we first evaluate the loss of energy by the α-particle on coming within the field of a normal hydrogen atom.

It is evident that the loss of energy by the α-particle on coming within the field, is equal to the gain of energy by the electron supposed to be initially at the 1*s* state. On account of this exchange energy the electron goes to some excited state or may be ionized.

The exchange energy ($\Delta$E) causing excitation of the normal electron at (100)-state to (*nlm*)-state is given by

$$\Delta \mathrm{E} = 2e^2 \int \frac{1}{r_{12}} \chi_{100} \chi_{nlm}\, \chi_1^{(\alpha)} \chi_2^{(\alpha)}\, d\tau_e\, d\tau_\alpha, \quad . \quad . \quad (1)$$

where $2e$ is the charge of the α-particle,

$$\chi_{100} = \mathrm{R}(r_1) = 2\left(\frac{z}{a}\right)^{3/2} e^{-\frac{zr_1}{a}}$$

$$\chi_{nlm} = \left(\frac{2z}{na}\right)^{3/2} \frac{\{(n-l-1)\,!\}^{1/2}}{(2n)^{1/2}\{(n+l)\,!\}^{3/2}} \cdot \left(\frac{2zr_1}{na}\right)^{l} \mathrm{L}_{n+l}^{2l+1}\left(\frac{2zr_1}{na}\right) e^{-\frac{zr_1}{na}} \times \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)\,!}{(l+m)\,!}} \cdot \mathrm{P}_l^m(\cos\theta_1) e^{im\phi_1},$$

$a$ being the radius of the first Bohr orbit for hydrogen and $r_{12}$ the distance between the electron (denoted by suffix 1), and the α-particle (denoted by the suffix 2) is given by

$$\frac{1}{r_{12}} = \frac{1}{[r]} \Sigma x^\nu \mathrm{P}_\nu(\cos\Theta),$$

in which $$x = \frac{r_1}{r_2}, \quad [r] = r_2 \quad \text{if} \quad r_2 > r_1,$$

$$x = \frac{r_2}{r_1}, \quad [r] = r_1 \quad \text{if} \quad r_1 > r_2,$$

* Blackett, Proc. Roy. Soc. cxxxv. p. 132 (1932).

and

$$P_\nu(\cos\Theta) = \sum_{-\nu}^{+\nu}(\mu)\frac{(\nu-|\mu|)!}{(\nu+|\mu|)!}P_\nu^\mu(\cos\theta_1)P_\nu^\mu(\cos\theta_2)e^{i\mu\phi_1}e^{i\mu\phi_2}$$

Since the $\alpha$-waves are supposed to be moving along the $x$-axis, we take (as $k$ is nearly the same before and after impact)

$$\chi_1^{(\alpha)}=\chi_2^{(\alpha)}=Ae^{ikx}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$k=\frac{2\pi}{\lambda}=\frac{2\pi Mv}{h}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

M, $v$ being the mass and the velocity of the $\alpha$-particle. Also we have $d\tau_e=r_1^2\,dr_1\sin\theta_1 d\theta_1 d\phi_1$ and $d\tau_\alpha=r_2^2\,dr_2\sin\theta_2 . d\theta_2\, d\phi_2$.

It may be seen without difficulty that $\phi_1$-integration of (1) gives zero except for $\mu=m$, $\theta_1$-integration vanishes except for $\nu=l$, and $\phi_2$-integration leads to zero except for $m=0$. On carrying out integrations with respect to $\phi_1$, $\theta_1$, and $\phi_2$, remembering the above conditions, we get from (1)

$$\Delta E=\frac{32\pi z^3e^2}{a^3}\sqrt{\frac{\pi}{2l+1}}\cdot\frac{\{(n-l-1)!\}^{1/2}}{n^2\{(n+l)!\}^{3/2}}$$
$$\times\int\chi_1^{(\alpha)}\chi_2^{(\alpha)}P_l(\cos\theta_2)r_2^2\,dr_2\sin\theta_2\,d\theta_2$$
$$\times\int\frac{1}{[r]}x_l e^{-\frac{zr_1}{a}\left(1+\frac{1}{n}\right)}\left(\frac{2zr_1}{na}\right)^l L_{n+l}^{2l+1}\left(\frac{2zr_1}{na}\right)r_1^2\,dr_1. \quad . \quad . \quad . \quad . \quad (4)$$

Now we have from (2) on expanding

$$\chi_1^{(\alpha)}\chi_2^{(\alpha)}=A^2e^{2ikx}.=A^2\sum_s^{0,\infty}B_sP_s(\cos\theta_2), \quad . \quad . \quad (5)$$

where

$$B_s=i^s(2s+1)\sqrt{\frac{\pi}{4\pi r_2}}\cdot J_{s+\frac{1}{2}}(2kr_2).$$

It is obvious that with the value of $\chi_1^{(\alpha)}\,\chi_2^{(\alpha)}$ in (5), the integration of (4) with respect to $\theta_2$ vanishes except for $s=l$. Thus (4) becomes, after integration with respect to $\theta_2$,

$$\Delta E=i^l.\frac{32\pi^2z^3e^2A^2}{a^3\sqrt{(2l+1)k}}\cdot\frac{\{(n-l-1)!\}^{1\cdot2}}{n^2\{(n+l)!\}^{3/2}}$$
$$\times\int r_2^{-1/2}J_{l+1/2}(2kr_2)r_2^2\,dr_2$$
$$\times\int\frac{1}{[r]}x^l e^{-\frac{zr_1}{a}\left(1+\frac{1}{n}\right)}.\left(\frac{2zr_1}{na}\right)^l.L_{n+l}^{2l+1}\left(\frac{2zr_1}{na}\right)r_1^2\,dr_1. \quad (6)$$

By selection rule $l=1$; so that (6) takes the simple form

$$\Delta E = i\frac{32\pi^2 z^3 e^2 A^2}{a^3\sqrt{3k}}\frac{\{(n-2)!\}^{1/2}}{n^2\{(n+1)!\}^{3/2}}\int r_2^{-1/2} J_{3/2}(2kr_2) r_2^2\, dr_2$$
$$\times \int \frac{x}{[r]} e^{-\frac{zr_1}{a}\left(1+\frac{1}{n}\right)} \cdot \frac{2zr_1}{na} \cdot L^3_{n+1}\left(\frac{2zr_1}{na}\right) \cdot r_1^2 dr_1. \quad . \quad (7)$$

Now the α-particles, on coming within the atomic field, never come up to the centre of the nucleus. From the classical dynamics the minimum distance of approach is evidently the distance of the vertex of the hyperbolic orbit from the nuclear centre; and it has the value

$$r_0 = \frac{2ze^2}{Mv^2}\left(\operatorname{cosec}\frac{\theta}{2}+1\right), \quad . \quad . \quad . \quad . \quad (8)$$

where $ze$ is the nuclear charge, $\theta$ the angle of scattering, M the mass of the α-particle, and $v$ its velocity.

It is clear that the α-wave which is associated with the α-particle cannot also reach the centre of the atom. In fact a spherical volume of radius $r_0$ remains undisturbed by the α-wave. Strictly the limiting radius $r_0$ should be determined wave-statistically; but in the absence of such a value we have to fall back on the dynamical value given in (8). It is noteworthy that the above idea of excluded region was previously used by Mukherjee * and Ghosh † to deduce some interesting formulæ for scattering.

Thus the lower limit of $r_2$-integration should be $r_0$ instead of zero. Hence (7) becomes

$$\Delta E = i\frac{32\pi^2 z^3 e^2 A^2}{a^3\sqrt{3k}}\frac{\{(n-2)!\}^{1/2}}{n^2\{(n+1)!\}^{3/2}}(I_1+I_2), \quad . \quad . \quad (9)$$

where

$$\underset{r_0<r_1}{I_1} = \int_{r_0}^{\infty} J_{3/2}(2kr_2) r_2^{3/2} dr_2^2 \cdot$$
$$\cdot \frac{1}{r_2^2}\int_0^{r_2}\left(\frac{2zr_1}{na}\right) L^3_{n+1}\left(\frac{2zr_1}{na}\right) e^{-\frac{zr_1}{a}\left(1+\frac{1}{n}\right)} r_1^3 dr_1, \quad (10)$$

$$\underset{r_1>r_2}{I_2} = \int_{r_0}^{\infty} J_{3/2}(2kr_2) r_2^{3/2} dr_2$$
$$\cdot r_2 \int_{r_2}^{\infty}\left(\frac{2zr_1}{na}\right) \cdot L^3_{n+1}\left(\frac{2zr_1}{na}\right) \cdot e^{-\frac{zr_1}{a}\left(1+\frac{1}{n}\right)} dr_1. \quad (11)$$

* K. K. Mukherjee, *Phys. Zeit.* xxxiv. p. 175 (1933).
† M. Ghosh, Phil. Mag. ser. 7, xx. p. 234 (1935).

Now it is well known that the Laguerre polynomial

$$L^3_{n+1}\left(\frac{2zr_1}{na}\right)=(-1)^{n+1}\left[(n+1)n(n-1)\left(\frac{2z}{na}\right)^{n-2}r_1^{n-2}\right.$$
$$-\frac{n(n-1)(n-2)(n+1)^2}{\lfloor 1}\left(\frac{2z}{na}\right)^{n-3}r_1^{n-3}$$
$$\left.+\ldots\frac{(-1)^{n-2}(n+1)^2\ldots4^2.3.2}{\underline{n-1}}\right].$$

Thus on putting $\alpha=\frac{z}{a}\left(1+\frac{1}{n}\right)$ we have from (10) and (11), on integrating term by term and neglecting the smaller terms,

$$\underset{r_0<<a}{I_1}=-\frac{a^4\sin 2kr_0}{z^4r_0}\cdot\frac{1-e^{-\alpha r_0}}{\sqrt{4\pi k^3}}\cdot G_1(n), \quad . \quad (12)$$

where

$$G_1(n)=(-1)^{n+1}\cdot\frac{2}{n+1}\left(\frac{n}{n+1}\right)^4$$
$$\times\left[(n+1)n(n-1)\left(\frac{2}{n+1}\right)^{n-2}\underline{n+2}\right.$$
$$-\frac{n(n-1)(n-2)(n+1)^2n^2}{\lfloor 1}\left(\frac{2}{n+1}\right)^{n-3}\underline{n+1}$$
$$+\frac{(n-1)(n-2)(n-3)(n+1)^2n^2}{\lfloor 2}\left(\frac{2}{n+1}\right)^{n-4}\underline{n}$$
$$\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\left.+(-1)^{n-2}\cdot\frac{3.2(n+1)^2n^2\ldots4^2}{\underline{n-2}}\underline{4}\right]$$

and

$$\underset{r_0>>a}{I_1}=(-1)^{n+1}\cdot\frac{e^{-\alpha r_0}\sin 2kr_0\cdot r_0{}^3}{\sqrt{4\pi k^3}}\cdot\frac{2}{n+1}$$
$$\times\left[(n+1)n(n-1)(r_0\beta)^{n-2}\right.$$
$$-\frac{n(n-1)(n-2)(n+1)^2}{\lfloor 1}(r_0\beta)^{n-3}+\ldots$$
$$\left.+(-1)^{n-2}\cdot\frac{(n+1)^2n^2\ldots4^2.3.2}{\lfloor n-2}\right], \quad . \quad . \quad (13)$$

where $$\beta=\frac{2z}{na}.$$

In obtaining the above values of $I_1$ by neglecting smaller terms we have supposed that $r_0k>>1$. This is evidently justified, since $k\sim10^{12}$ and $r_0$ should be $\sim10^{-8}\rightarrow10^{-9}$. Remembering the above assumption, we have for $I_2$ :—

$$\underset{r_0<<a}{I_2} = -\frac{ar_0^2 \sin 2kr_0}{z} \cdot \frac{e^{-\alpha r_0}}{\sqrt{4\pi k^3}} \cdot G_2(n), \quad . \quad (14)$$

where

$$G_2(n)=(-1)^{n+1} \cdot \frac{2}{n+1} \cdot \frac{n}{n+1} \times\left[(n+1)n(n-1)\left(\frac{2}{n+1}\right)^{n-2}\frac{1}{\underline{n-1}}\right.$$

$$-\frac{n(n-1)(n-2)(n+1)^2}{\underline{1}}\left(\frac{2}{n+1}\right)^{n-3}\frac{1}{\underline{n-2}}+\ldots$$

$$\left.+(-1)^{n-2}\frac{(n+1)^2n^2\ldots4^2.3.2}{\underline{n-2}}\right]$$

and

$$\underset{r_0>>a}{I_2} = -\underset{r_0>>a}{I_1} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus from (9) we find that $\Delta E=0$ for the case when $r_0>>a$. This is rather interesting, for it follows from general consideration that there can be no loss of energy unless the α-particles penetrate the $k$-shell at $r=a$. We are then left with the case $r_0<<a$, and we have from (9), on substituting for $I_1$, $I_2$ from (12) and (14),

$$\Delta E=-i\frac{16\pi^2z^2e^2A^2}{\sqrt{3\pi}\,.\,k^2a^2} \cdot \frac{\sin 2kr_0}{r_0} \frac{\{(n-2)!\}^{1/2}}{n^2\{(n+1)!\}^{3/2}}$$

$$\cdot\left\{\frac{a^3}{z^3}(1-e^{-\alpha r_0})G_1(n)+r_0^3e^{-\alpha r_0}G_2(n)\right\}. \quad (16)$$

Now since $a>>r_0$, we may neglect the second term involving $G_2(n)$ in comparison with the first. Hence we have, taking $z=1$ for hydrogen and $\sqrt{3\pi}\sim3$,

$$\Delta E=-i\frac{16\pi^2e^2A^2}{3k^2}$$

$$\cdot\frac{a\sin 2kr_0}{r_0}(1-e^{-\alpha r_0})\frac{\{(n-2)!\}^{1/2}}{n^2\{(n+1)!\}^{3/2}}G_1(n). \quad (17)$$

Again, since $1-e^{-\alpha r_0}\sim\alpha r_0$ and $\alpha a=\frac{n+1}{n}$, (17) becomes

$$\Delta E=-i\frac{16\pi^2e^2A^2}{3k^2}\sin 2kr_0F_1(n), \quad . \quad . \quad . \quad (18)$$

where $$F_1(n)=\frac{n+1}{n^3}\frac{\{(n-2)!\}^{1/2}}{\{(n+1)!\}^{3/2}}G_1(n). \quad . \quad . \quad (19)$$

Now from (2) we have for the averaging condition per unit cross-section of the beam

$$A^2\int_0^\infty e^{\pm 2ikz}\,dx=1,$$

which gives $A^2=\mp 2ik$. On substituting this value of $A^2$ in (18) we have for the loss of energy by the $\alpha$-particle

$$\Delta E=\frac{32\pi^2e^2}{3k}\sin 2kr_0F_1(n). \quad . \quad . \quad . \quad (20)$$

As $n$ must have all possible values from $n=2$ to $\infty$, we have to evaluate $\overset{2,\infty}{\underset{n}{\Sigma}}F_1(n)$, in order to get the total loss of energy due to excitation of the $k$-electron. We find that $\overset{2,\infty}{\underset{n}{\Sigma}}F_1(n)=1\cdot004$, being correct up to the second place of decimal. Thus the total loss of energy through excitation is

$$\Delta E=\frac{32\pi^2e^2}{3k}\sin 2kr_0. \quad . \quad . \quad . \quad . \quad (21)$$

*Ionization.*—It is evident that because formula (21) includes values of $n$ up to infinity the loss of energy considered there should be both due to excitation and ionization. However, it may be useful to derive the latter independently.

The procedure is more or less the same as before. The exchange energy in the present case is given by (1), if one only puts $\chi_{hyp.}$ in place of $\chi_{nlm}$, where

$$\left.\begin{aligned}\chi_{hyp.}&=R_{hyp.}\sqrt{\frac{2l+1}{4\pi}\cdot\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta_1)e^{im\phi_1},\\ R_{hyp.}&=C\cdot\frac{e^{-\frac{ir_1}{a}}}{r_1}\ \text{(approx.)},\end{aligned}\right\} \quad . \quad (22)$$

in which $a$ is the radius of the first Bohr orbit for hydrogen.

We have, corresponding to (4),

$$\Delta E = \frac{16\pi z^{3/2}e^2}{a^{3/2}}\sqrt{\frac{\pi}{2l+1}}\cdot C\int\chi_1^{(\alpha)}\chi_2^{(\alpha)}P_l(\cos\theta_2)r_2^2\,dr_2\sin\theta_2\,d\theta_2 \times\int\frac{1}{[r]}x^l e^{-\frac{zr_1}{a}}e^{\frac{ir_1}{a}}r_1\,dr_1. \quad (23)$$

On integrating with respect to $\theta_2$ we have, corresponding to (7), for $l=1$,

$$\Delta E = i\frac{16\pi^2 z^{3/2}e^2A^2}{a^{3/2}\sqrt{3k}}\cdot C\int r_2^{-1/2}J_{3/2}(2kr_2)r_2^2\,dr_2 \times\int\frac{x}{[r]}e^{-\frac{zr_1}{a}}e^{\frac{ir_1}{a}}r_1\,dr_1. \quad (24)$$

Or we have

$$\Delta E = i\frac{16\pi^2 z^{3/2}e^2A^2}{a^{3/2}\sqrt{3k}}\cdot c(I_3+I_4), \quad . \quad . \quad . \quad (25)$$

where

$$\underset{r_1<r_2}{I_3} = \int_{r_0}^{\infty}J_{3/2}(2kr_2)r_2^{3/2}\,dr_2\cdot\frac{1}{r_2^2}\int_0^{r_2}e^{-\frac{zr_1}{a}}e^{\frac{ir_1}{a}}r_1^2\,dr_1, \quad (26)$$

$$\underset{r_1>r_2}{I_4} = \int_{r_0}^{\infty}J_{3/2}(2kr_2)r_2^{3/2}\,dr_2\cdot r_2\int_{r_2}^{\infty}e^{-\frac{zr_1}{a}}e^{\frac{ir_1}{a}}\cdot\frac{1}{r_1}dr_1. \quad . \quad (27)$$

Making approximations as before, using the inequality $r_0k>>1$, we have

$$\underset{r_0<<a}{I_3} = -2a^2\cdot\frac{\sin 2kr_0}{\sqrt{4k^3}}\cdot\frac{z(z^3-3z)}{(1+z^2)^3}, \quad . \quad . \quad (28)$$

$$\underset{r_0>>a}{I_3} = \frac{\sin 2kr_0}{\sqrt{4\pi k^3}}\cdot\frac{ar_0}{1+z^2}\left(z\cos\frac{r_0}{a}-\sin\frac{r_0}{a}\right). \quad (29)$$

It may be shown without difficulty that

$$\underset{r_0<<a}{I_4} = -\frac{\sin 2kr_0}{\sqrt{4\pi k^3}}\cdot\frac{ar_0}{1+z^2}\left(z\cos\frac{r_0}{a}-\sin\frac{r_0}{a}\right), \quad (30)$$

and the asymptotic value of $I_4$ is

$$\underset{r_0>>a}{I_4} = -\underset{r_0>>a}{I_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Thus we find from (25) that $\Delta E=0$ for the case $r_0>>a$, as it should be. It is also evident that in the case $r_0<<a$,

$I_4 << I_3$. Therefore we have from (25), on taking $z=1$ and $\sqrt{3\pi} \sim 3$,

$$\Delta E = i \frac{4\pi^2 e^2 A^2 a^{1\,2}}{3k^2} \cdot C \sin 2kr_0. \quad . \quad . \quad . \quad (32)$$

The constant C may be evaluated from the following average-condition :

$$C^2 \int_0^\infty \frac{e^{\frac{2ir}{a}}}{r^2} \cdot r^2\, dr = 1.$$

Remembering that C is partly real and partly imaginary, the above may be written as

$$C_1^2 \int_0^\infty e^{\frac{2ir}{a}} e^{-i\theta}\, dr = 1.$$

Or, neglecting the imaginary part,

$$C_1^2 \int_0^\infty \cos\left(\frac{2r}{a} - \theta\right) dr = 1,$$

which gives on integration $\sqrt{C_1^2} \sin \theta = \sqrt{2}/a$. Taking this as the value of C, we have from (32), on substituting for $A^2$ already evaluated,

$$\Delta E = \frac{8\sqrt{2}\pi^2 e^2}{3k} \sin 2kr_0, \quad . \quad . \quad . \quad . \quad (33)$$

which is less than the value given in (21) determining the total loss of energy due to excitation and ionization.

*Calculation of range.*—On travelling through a distance $dx$ the α-particle meets with $Ndx$ hydrogen atoms. Thus the total loss of energy on travelling through $dx$ is

$$\Delta T = -Ndx \,.\, \Delta E = -\frac{32N\pi^2 e^2}{3k} \sin 2kr_0 \,.\, dx, \quad . \quad (34)$$

being different from the results of the previous workers, all of whom obtain the loss of energy as a logarithmic function of velocity, etc.

On substituting for $k$ and $r_0$ from (3) and (8), we have from (34)

$$\frac{dT}{dx} = -\frac{16\pi N e^2 h}{3Mv} \sin\left\{\frac{4\pi e^2}{hv}\left(\operatorname{cosec}\frac{\theta}{2} + 1\right)\right\}. \quad (35)$$

Now, as already pointed out, $kr_0 >> 1$, so that $\frac{4\pi e^2}{hv}$

$.(\operatorname{cosec}\theta/2+1)>>1$. Therefore we may take the sine-factor in (35) as

$$\sin\left\{\frac{4\pi e^2}{h\upsilon}\left(\operatorname{cosec}\frac{\theta}{2}+1\right)-s\pi\right\}.$$

where $s$ is such that the angle falls within the first quadrant. Thus on expanding we have from (35)

$$\frac{dT}{dx}=\frac{A}{v}+\frac{B}{v^2}+O\left(\frac{1}{v^3}\right), \quad . \quad . \quad . \quad . \quad (36)$$

where

$$A=\frac{16\pi^2 Nse^2h}{3M}, \quad B=-\frac{64\pi^2 Ne^4}{3M}\left(\operatorname{cosec}\frac{\theta}{2}+1\right).$$

If we restrict only to the first term, then on integrating (36) we get for the range (R), since $T=\frac{1}{2}Mv^2$,

$$R\propto v^3.$$

On the other hand, the second term gives $R\propto v^4$. As A and B are nearly of the same order of magnitude it is difficult to decide between the $v^3$- and the $v^4$-law. It would, however, seem desirable to take Geiger's law in the general form :

$$R=\ldots+a_2v^2+a_3v^3+a_4v^4+a_5v^5+\ldots, \quad (37)$$

as suggested by the higher order terms.

It may be remarked, in conclusion, that in (36) B is very large, and consequently $\theta$, the angle of scattering, is very small. Thus the phenomenon under discussion is due to small angle scattering of the $\alpha$-particles. On assuming the $v^4$-law the angle of scattering may be calculated theoretically.

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March 1936.

XXII. *A Glow Discharge.* *By* F. H. Newman, *D.Sc., F.Inst.P., Professor of Physics in the University College of the South-West of England, Exeter* *.

AN arc is differentiated from a glow discharge primarily by the current density at the cathode and the magnitude of the cathode fall. Whereas in a glow discharge the current density at the cathode is normally

* Communicated by the Author.

a small fraction of an ampere per sq. cm. and the cathode fall is usually greater than 100 volts, in an arc the current density at that part of the cathode which is carrying the current is high, probably over a thousand amperes per sq. cm., the cathode fall generally ranging from 5 to 20 volts. In a glow discharge most of the current is borne by the positive ions and a small percentage by free electrons leaving the cathode; but the current in the arc is mainly carried by the cathodic electrons, and only a small fraction by the positive ions striking the cathode.

Güntherschulze and Fricke * investigated a new kind of glow discharge which exhibited no dark space or cathode fall of potential. The results of experiments carried out with many cathodic materials showed that the conditions necessary for obtaining this type of glow discharge are that the cathode must consist of two parts: (*a*) a material of which the specific resistance lies between that of graphite and a semi-conductor, and (*b*) a thin coating of a very highly insulating material. With this arrangement the potential difference on discharge may be much less than the normal values of the cathode fall for a glow discharge. The suggested explanation is that the electrons are ejected from the cathode with a velocity corresponding to 20–30 volts, and they enter the gas with a velocity almost as great as that due to the potential difference across the film of insulating material.

Druyvesteyn † suggested that the electronic emission from the cathode of an arc may be similar to the mechanism in this type of glow discharge. If some areas on the cathode are covered with a thin layer of an insulator—say $10^{-4}$ or $10^{-5}$ cm. thick—the positive ion space-charge at the insulator gives rise to a high field near the cathode metal and electrons enter the gas with a high velocity. Thus the greater part of the cathode drop exists across the insulator and the high field is explained.

In connexion with these theories it is interesting to note that a similar glow had been described by the author ‡ some years ago in connexion with work on the mechanism of the arc. Recently this glow has been produced

† *Zeits. f. Phys.* lxxxvi. pp. 451, 821 (1933).
† 'Nature,' cxxxvii. p. 580 (1936).
‡ Phil. Mag. ii. p. 796 (1926); vi. p. 811 (1928); vii. p. 1090 (1929).

occasionally with the carbon arc, but is best seen if iron-arc electrodes are employed. In the previous work these iron electrodes were spaced a few millimetres apart in a vacuum and a steady potential difference applied across them. On passing a momentary electric discharge between one of the arc electrodes and a third one a brilliant white glow was produced. The arc electrodes remained cold, and it was impossible to produce the glow in the absence of any applied potential difference. The gas-pressure was so low that the electrical discharge gave no luminosity within the tube, and the glow could be produced with residual air or hydrogen at pressures below $10^{-3}$ mm. of mercury. Although the spectra of the radiations from the glow and arc in hydrogen were similar, the former showed little trace of the secondary lines of hydrogen. Another type of glow was obtained with residual helium and neon. If the arc in these gases was interrupted, and the potential difference immediately reapplied across the arc electrodes, a blue glow appeared in the vicinity of the cathode. It was much fainter than the glow in hydrogen, and only persisted for a short interval.

As mentioned above, the glow discharge has been obtained recently with carbon electrodes, but the necessary conditions for its production have not been determined. The potential difference across the arc terminals shows no change when the glow is formed, whereas when the arc proper strikes, the potential difference drops instantaneously to a lower value appropriate to the strength of the current. Efforts to show that this glow initiates the carbon arc have been unsuccessful owing to the instantaneous starting of the arc, but the experiments support Druyvesteyn's hypothesis.

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## XXIII. *Attempt to detect Radioactivity produced by Positrons.*

*By* Prof. G. P. Thomson, *F.R.S.*, and J. A. Saxton, *Imperial College of Science and Technology* *

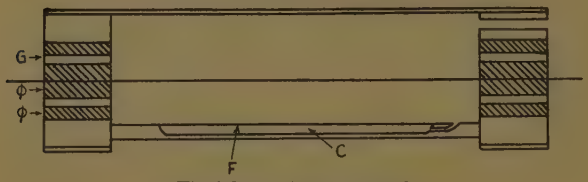
WHILE nuclear disintegrations have been produced by the impact of a variety of particles of atomic mass, no cases are known in which such disintegrations

* Communicated by the Authors.

are caused by electrons or positrons. It is difficult to detect such effects if they are instantaneous because the X-rays caused by the electrons would mask them. In view, however, of the discovery of induced radioactivity it seemed worth trying if this could be produced by the impact of light particles. Positrons seem the most promising, for one would expect the atomic electrons to have already produced any change needing electrons only *.

The experiment took the form of irradiating various substances placed inside a Geiger counter with positrons produced in lead by the materialization of the hard $\gamma$-rays from a radiothorium source. After a certain time, usually five minutes, the source was removed and measurements made to see if the initial number of discharges in the counter exceeded the normal rate. The

Fig. 1.




Final form of counter used.

G. Aluminium guard-ring (at earth potential).
$\phi$. Quartz insulation.
F. Gold foil.
C. Chamber for irradiated specimens.

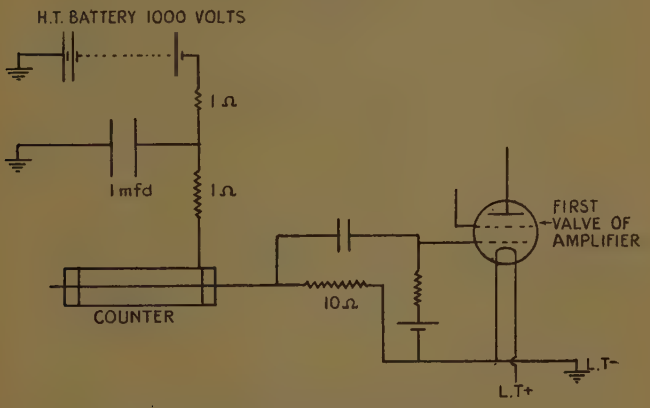
counters were of the cylindrical wire type $8 \times 2$ cm., with axis horizontal, and the substance to be irradiated was placed in a hollow on the inside of the lower part of the aluminium case of the counter covered by a thin gold film approximately $10^{-5}$ cm. thick, to prevent its interfering with the working of the counter, which contained air at a few centimetres pressure.

The first experiments seemed to show a positive effect with some substances, the count in the first minute after removing the source being larger than the average of the

* The experiments recorded here were made in 1935 ; their publication has been delayed by the illness of one of the authors. Similar experiments, but using electrons, have been published by Livingood and Snell, Phys. Rev., December 1935, also with negative results.

next four minutes. Blank tests, however, in which the counter was merely allowed to rest for a few minutes between experiments without applied voltage (the source being entirely removed), showed an almost equal effect, and it appears to be due to changes in the electrical state of the insulation when the voltage is applied Ebonite insulation was used in these experiments. It was thought probable that the strong ionization produced by the source in the counter might upset its behaviour if the high tension was left on during the irradiation (see below), and it was therefore disconnected.

Fig. 2.




Counter and first valve circuit.

Apparently on switching on again it takes about a minute before the distribution of charge in the ebonite reaches a steady state, causing a slight change in the natural count. Thus with borax in the counter a series of experiments gave a ratio of the count in the first minute after irradiation to that in the next four of 1·092 with a statistical standard deviation of $\pm$·041, while a similar series without irradiation gave 1·055$\pm$·032. The difference, though in the right direction for a true effect, is too small to be significant.

A new counter was then made using quartz insulation with an earthed guard-ring, which gave the following

results for the ratio of the first minute to the mean of the next three :—

| | |
|---|---|
| No irradiation | $1{\cdot}036 \pm {\cdot}046$ |
| Aluminium counter irradiated | $1{\cdot}048 \pm {\cdot}043$ |
| Aluminium counter with graphite irradiated | $\cdot 993 \pm {\cdot}057$ |
| Aluminium counter with sodium fluoride irradiated | $\cdot 991 \pm {\cdot}076$ |
| Mean of irradiated experiments | $1{\cdot}022 \pm 0{\cdot}032$ |

There is still a trace of an effect even with the blank runs, but no evidence at all for any induced radioactivity, since if the aluminium of the counter were active it should produce an effect even in the presence of other substances. The following Table gives the results with the ebonite counter. When compared with those for the blank

| Substance in counter. | Total count in 1st minute. | Mean of next 4. | Ratio $\frac{\text{First min.}}{\text{Mean of next 4.}}$ |
|---|---|---|---|
| Borax | 927 | 848·5 | $1{\cdot}092 \pm 0{\cdot}041$ |
| $B_2O_3$ | 441 | 427·6 | $1{\cdot}031 \pm 0{\cdot}054$ |
| Be | 521 | 530 | $0{\cdot}983 \pm 0{\cdot}047$ |
| MgO | 398 | 389·8 | $1{\cdot}021 \pm 0{\cdot}056$ |
| LiF | 468 | 484·1 | $0{\cdot}967 \pm 0{\cdot}043$ |
| Graphite | 404 | 377 | $1{\cdot}072 \pm 0{\cdot}058$ |
| NaF | 492 | 455·6 | $1{\cdot}080 \pm 0{\cdot}043$ |
| Blank run | 1409 | 1335 | $1{\cdot}055 \pm 0{\cdot}032$ |

runs, they are about what would be expected in the absence of any radioactive effect. The average count was about 12 per min.

*Fatigue of Counter.*—In making the above experiments care was taken to switch on the high tension battery first, then the thyratron connexions, and start the count 3–4 seconds later, thus avoiding initial disturbances. We tried to investigate the cause of the apparent blank effect by a series of experiments in which the counter was powerfully irradiated with the high tension connected before the count was taken. The following results show that in these circumstances a counter becomes fatigued recovering after a time of the order of a minute. Since the effect occurs equally with air and argon it is

apparently not due to chemical changes in the gas. It may be due to charges distributed on the insulator.

| | Ratio $\left\{\frac{\text{First min.}}{\text{Mean of next 3.}}\right.$ |
|---|---|
| Counter filled with air ..... | $0{\cdot}920 \pm 0{\cdot}041$ |
| Counter filled with argon ..... | $0{\cdot}937 \pm 0{\cdot}043$ |

*Sensitivity of Experiments.*—The following calculation gives, in order of magnitude, the least cross-section for collision between positron and nucleus corresponding to the production of a hypothetical radioactive substance which could have been detected in these experiments. The strength of the source in equivalent milligrams of radium as measured by its $\gamma$-rays was 16·88 at the beginning of the experiments and 13·71 at the end. The positrons are produced mainly by the 2·6 million volt $\gamma$-ray from ThC″. For equal $\gamma$-ray activity a thorium source emits $\cdot 77 \times \frac{35}{65} = \cdot 41$ as many $\gamma$'s as the radium source does 7 cm. $\alpha$-particles *, assuming that each ThC″ transformation gives one 2·6 M.V. $\gamma$-ray. Hence from a 15 milligram source the number of $\gamma$'s is $3{\cdot}7 \times 10^7 \times 15 \times \cdot 41 = 2{\cdot}3 \times 10^8$ per second. The absorption coefficient of the $\gamma$'s in lead is $\mu/\rho = \cdot 041$. The range of the positrons produced is about † 0·67 gm./sq. cm. as a maximum, or say ·5 mm. of lead. In this thickness, $1 - e^{0{\cdot}45 \times 0{\cdot}05} = \cdot 022$ of the $\gamma$'s are absorbed. Of these perhaps 15 per cent. produce positrons, and the geometry allows about 1 in 4 to enter the counter ; thus the number per second is $2{\cdot}3 \times 10^8 \times \cdot 022 \times \cdot 25 \times \cdot 15 = 1{\cdot}9 \times 10^5$. The natural count was round about 12 a minute, and an effect of about 1 extra in the first minute could have been detected. The positrons had sufficient energy to penetrate the layer of substance being tested. In the most favourable case about $\frac{1}{8}$ of the disintegrating atoms might have affected the counter ; but this fraction would be reduced if the range of the product of disintegration was small. When equilibrium is reached the

* Shenstone and Schlundt ; see Rutherford, Chadwick, & Ellis, 'Radiations from Radioactive Substances,' p. 501.

† Chadwick, Blackett, & Occhialini, Proc. Roy. Soc. (A) cxliv. p. 235 (1934).

rate of dissociation is equal to the rate of production of radioactive atoms. If the yield per positron is $\alpha$, we get $1{\cdot}9\times10^5\times\alpha/3$ discharges per second at first. We are only concerned with periods of the order of 1 minute, though a few experiments in which the irradiation was continued overnight showed that there was no very large long-period effect. The excess for the first minute will be of the order of 20 times the initial rate, so that $1{\cdot}9\times10^5\times\alpha\times\frac{20}{3}<1$ or $\alpha<7{\cdot}7\times10^{-7}$. For the thickness used, about 0·5 mm. and in the case of carbon (atomic weight 12), this expression leads to a value of $1{\cdot}5\times10^{-28}$ cm.$^2$ for the least detectable absorption cross-section. This also represents an average value for the other elements investigated, which had atomic weights of the same order of magnitude. As there are about 10 electrons formed for each positron, the least detectable cross-section for electrons is about 1/10th of this, *i. e.*, $1{\cdot}5\times10^{-29}$ cm.$^2$. If radioactivity involving the emission of particles of electronic mass is always accompanied by the emission of neutrinos, it would be impossible to reverse the effect and obtain an absorption of electrons unless free neutrinos were also present. Thus the negative result we have obtained is to be expected on the neutrino hypothesis.

*Summary.*

Various substances of small atomic weight have been bombarded by positrons in an attempt to detect induced radioactivity. No such effect was found. Some abnormalities in the behaviour of counters are noted.

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XXIV. *Notes on Two-Dimensional Potential Theory.*—I. *The Force and Couple in Electrostatic Problems.* *By* Rosa M. Morris, *B.Sc.**

1. IT is already well known that in two-dimensional problems in hydrodynamics, relating to the streaming of liquid passed fixed obstacles, the forces and

* Communicated by Prof. G. H. Livens.

couple on the body can be expressed as simple contour integrals involving the complex potential function $\Omega$, where

$$\Omega = \phi + i\psi,$$

$\phi$ being the velocity potential and $\psi$ the stream function of the motion. It does not appear, however, to have been noticed that, although the boundary conditions * are essentially different, there are corresponding results for the force and couple on a cylindrical conductor in a two-dimensional electrostatic field. In fact if

$$\Omega = \phi + i\psi$$

is the complex potential function, where $\phi$ is the potential and $\psi$=const. are the lines of force, then the components of the resultant force on the cylinder per unit length can be found by the evaluation of

$$\frac{1}{8\pi}\int_c \left(\frac{\partial\Omega}{\partial z}\right)^2 dz,$$

and the couple by the evaluation of

$$\frac{1}{8\pi}\int_c \left(\frac{\partial\Omega}{\partial z}\right)^2 z\, dz,$$

both being integrated round the curve of the cross-section of the cylinder.

2. We know that the force per unit area at any point on a conducting body in an electric field is

$$2\pi\sigma^2$$

in the direction of the outward normal, $\sigma$ being the charge density at the point. In the case of a cylinder in the two-dimensional electric field, if X and Y represent the components of the resultant force per unit length in the direction of the axes, then

$$X = 2\pi\int_c \sigma^2 \frac{dy}{ds}\, ds,$$

$$Y = -2\pi\int_c \sigma^2 \frac{dx}{ds}\, ds,$$

integrated round $c$, the contour of the cross-section of the cylinder.

* In terms of the potential gradients themselves they are more similar. In the hydrodynamic case the complex potential is purely real on the surface, whereas in the electrical case it is purely imaginary.

Then $$Y+iX=-2\pi\int_c \sigma^2(dx-idy).$$

Now the forces are normal at the surface of the cylinder which is conducting, and therefore if $E_x$ $E_y$ denote the components of the electric force at any point of the surface we have

$$\frac{E_x}{dy}=\frac{E_y}{-dx}=\frac{E_x+iE_y}{-i(dx+idy)}=\frac{E_x-iE_y}{i(dx-idy)}=\frac{\sqrt{(E_x^2+E_y^2)}}{ds}.$$

Now $\Omega=\phi+i\psi$ being the complex potential,

$$\frac{\partial\Omega}{\partial z}=\frac{\partial\phi}{\partial x}+\frac{i\,\partial\psi}{\partial x}=-E_x+iE_y,$$

and also

$$4\pi\sigma=-\frac{\partial\phi}{\partial n}=-\frac{\partial\phi}{\partial x}\frac{dy}{ds}+\frac{\partial\phi}{\partial y}\frac{dx}{ds}$$
$$=E_x\frac{dy}{ds}-E_y\frac{dx}{ds}.$$

Thus

$$(4\pi\sigma)^2=E_x^2+E_y^2=-(E_x-iE_y)^2\frac{(dx+idy)}{(dx-idy)},$$

and therefore

$$Y+iX=\frac{1}{8\pi}\int_c (E_x-iE_y)^2(dx+idy)$$
$$=\frac{1}{8\pi}\int_c\left(\frac{\partial\Omega}{\partial z}\right)dz.$$

This integral also gives the force on any part of the cylinder, say between the points $z=z_1$ and $z=z_2$, if it is integrated along the corresponding part of the boundary curve between these points.

3. In a similar manner we can find the couple on the conducting cylinder. The force per unit area at the point $(x, y)$ on the cylinder has components

$$2\pi\sigma^2\frac{dy}{ds},\quad -2\pi\sigma^2\frac{dx}{ds}.$$

The couple on the cylinder in the positive sense round the axis is then given by

$$-2\pi\int_c \sigma^2(x\,dx+y\,dy).$$

We now prove that this is the real part of the contour integral

$$\frac{1}{8\pi}\int_c \left(\frac{\partial\Omega}{\partial z}\right)^2 z\,dz.$$

As before,

$$\left(\frac{\partial\Omega}{\partial z}\right)^2 z\,dz=(\mathrm{E}_x-i\,\mathrm{E}_y)^2(x+iy)\,(dx+i\,dy)$$

$$=-(\mathrm{E}_x-i\,\mathrm{E}_y)(\mathrm{E}_x+i\,\mathrm{E}_y)(x+iy)(dx-i\,dy)$$

$$=-(\mathrm{E}_x{}^2+\mathrm{E}_y{}^2)(x+iy)(dx-i\,dy).$$

The real part of this is

$$-(\mathrm{E}_x{}^2+\mathrm{E}_y{}^2)(x\,dx+y\,dy)=-(4\pi\sigma)^2(x\,dx+y\,dy),$$

so that the couple is as stated.

4. We may illustrate the use of the above results by considering the simple and well-known case of the elliptic cylinder in a uniform field.

We take the general case where the undisturbed field has its lines inclined at an angle $\theta$ with the $x$-axis, and defined therefore by the complex potential

$$\Omega_0=\phi_0+i\psi_0=-\mathrm{E}e^{-i\theta}z.$$

The elliptic cylinder being defined by the transformation

$$z=c\,\cos\,(\zeta+i\alpha):\eta=0,\quad\text{where}\quad\zeta=\xi+i\eta,$$

we have by the usual method the complex potential function of the complete field defined by

$$\Omega=\Omega_0+\mathrm{E}ce^{i\zeta}\cosh\,(\alpha+i\theta)$$

$$=-\mathrm{E}e^{\ i\theta}z+\mathrm{E}e^{\alpha}\{z-\sqrt{(z^2-c^2)}\}\cosh\,(\alpha+i\theta).$$

Thus

$$\frac{\partial\Omega}{\partial z}=-\mathrm{E}e^{-i\theta}+\mathrm{E}e^{\alpha}\cosh\,(\alpha+i\theta)\left\{1-\frac{z}{\sqrt{(z^2-c^2)}}\right\}$$

$$=-\mathrm{E}e^{-i\theta}+\mathrm{E}e^{\alpha}\cosh\,(\alpha+i\theta)\,\frac{c^2}{2z^2}\cdots.$$

The force on the whole cylinder is given by the simple contour

$$\mathrm{Y}+iX=\frac{1}{8\pi}\int_c\left(\frac{\partial\Omega}{\partial z}\right)^2 dz,$$

and is easily seen to be zero.

The force on the part of the surface of the cylinder between the points $z=z_1$ and $z=z_2$ on its boundary has components X and Y, where

$$Y+iX=\frac{1}{8\pi}\int_{z_1}^{z_2}\left\{A-\frac{Bz}{\sqrt{(z^2-c^2)}}\right\}^2 dz,$$

where we have written

$$\frac{\partial\Omega}{\partial z}=A-\frac{Bz}{\sqrt{(z^2-c^2)}}, \qquad A=Ee^{\alpha}\sinh(\alpha+i\theta),$$
$$B=Ee^{\alpha}\cosh(\alpha+i\theta).$$

This gives

$$\begin{aligned}Y+iX&=\frac{1}{8\pi}\int_{z_1}^{z_2}\left\{A^2-\frac{2ABz}{\sqrt{(z^2-c^2)}}+\frac{B^2z^2}{z^2-c^2}\right\}dz\\&=\frac{1}{8\pi}\int_{z_1}^{z_2}\left\{A^2+B^2-\frac{2ABz}{\sqrt{(z^2-c^2)}}+\frac{B^2c^2}{z^2-c^2}\right\}dz\\&=\frac{1}{8\pi}\Big[(A^2+B^2)(z_2-z_1)\\&\qquad -2AB\{\sqrt{(z_2^2-c^2)}-\sqrt{(z_1^2-c^2)}\}\\&\qquad +\frac{B^2c}{2}\log\left(\frac{z_2-c}{z_2+c}\cdot\frac{z_1+c}{z_1-c}\right)\Big],\end{aligned}$$

a result which takes simple forms in certain special cases which we need not further elaborate.

5. The couple about the axis on the complete cylinder is the real part of

$$\begin{aligned}&\frac{1}{8\pi}\int_c\left(\frac{\partial\Omega}{\partial z}\right)^2 z\,dz\\&=\frac{1}{8\pi}\int_c\left\{-Ee^{-i\theta}+Ee^{\alpha}\cosh(\alpha+i\theta)\frac{c^2}{2z^2}\cdots\right\}^2 z\,dz,\end{aligned}$$

and this gives

$$-\frac{iE^2e^{\alpha-i\theta}c^2\cosh(\alpha+i\theta)}{4}.$$

The couple is the real part or

$$\frac{c^2E^2\sin 2\theta}{8},$$

which is the usual and familiar result.

It is not always possible in more complex problems to express the contour integrals as above in a suitable or simple form. In some of these cases, however, the corresponding complex integrals in the $\zeta$-plane, are more tractable—although they are not integrals round complete contours,—and it is possible to determine the force and couple by a process which is still simpler than the more usual one involving real functions only. We may return to this point in a later note.

Cardiff,
Nov. 4th, 1936.

## XXV. *The Temperature of Open Flames.* *By* Prof. W. T. David *.

OBSERVERS who have measured the temperature of the Bunsen flame at various points along its axis by the sodium-line reversal method report that a steep "temperature gradient" exists over a very short distance in the immediate neighbourhood of the inner cone, but that after this there is a remarkably uniform temperature for a considerable distance. Thus Griffiths and Awbery in a flame of 14 inches total height found a steady temperature for some 4 inches above the inner cone †. A diagrammatic representation of the sodium temperatures is shown in fig. 1.

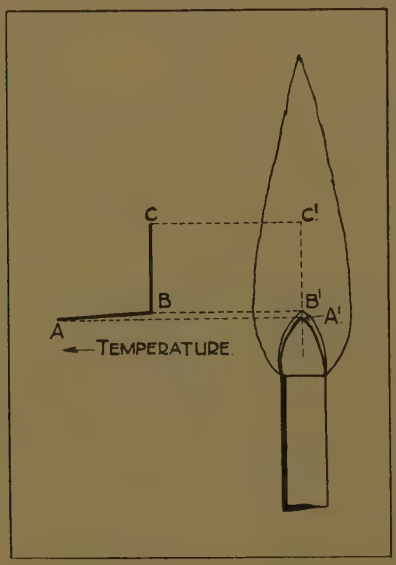
Measurements by Hartley of the radiation from flames ‡ and radiation measurements in explosions § make it clear that heat loss by radiation over the short distance A′B′ is very small (of the order of one per cent. of the heat of combustion), and it is obvious that the steep gradient of temperature found by the sodium method cannot be a gradient of true temperature (which throughout this paper is assumed to be proportional to the mean molecular translational energy). It is probable that the sodium atoms in this region acquire a high degree of excitation as a result of the intense chemical activity proceeding there, and that consequently the temperature measure-

* Communicated by the Author.
† Proc. Roy. Soc. A, lxxiii. p. 401 (1929).
‡ Communications No. 63, Inst. Gas Engineers, 1932, p. 22.
§ Phil. Mag. xvii. p. 179 (1934).

ments they yield have no very obvious relation to the true temperatures obtaining.

The sodium measurements which have the best claim to be regarded as the true temperature of flame resulting from the combustion of the mixture fed to the burner are those made within the region B′C′, in which chemical equilibrium would appear to have been established and in which, as has been stated, the temperature remains steady.

Fig .1.

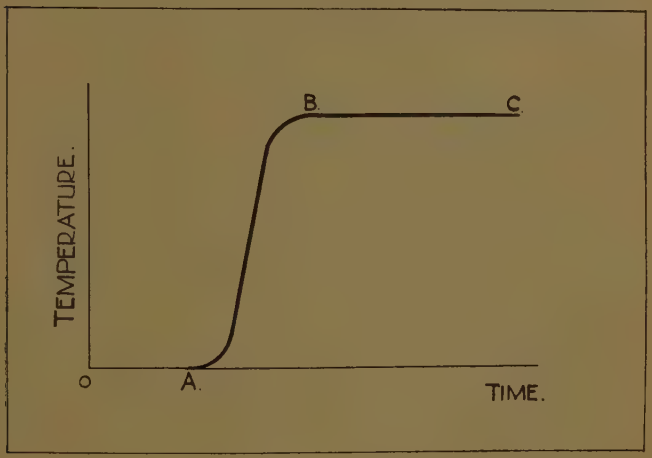



It is of interest to compare the sodium temperatures in this region with those obtained by means of platinum thermometry. These latter were measured during the "pre-pressure interval" in closed vessel explosions. A thin platinum-rhodium wire (0·0005 inch in diameter) was placed near the igniting spark. As the flame spread outwards from the spark it met the wire and rapidly heated it up. The wire thereafter remained immersed in the burnt gases and its temperature (as inferred from its resistance) remained perfectly steady for as long as

the pre-pressure interval lasted. A typical continuous record taken photographically is shown in fig. 2. At o the spark was passed, at A the flame reached the wire, and BC shows the steady temperature of the wire as it remained immersed in the burnt gases.

For any given inflammable gaseous mixture this steady temperature BC should clearly compare with the steady sodium temperature BC (fig. 1) when a similar mixture is fed to the burner.

Fig. 2.

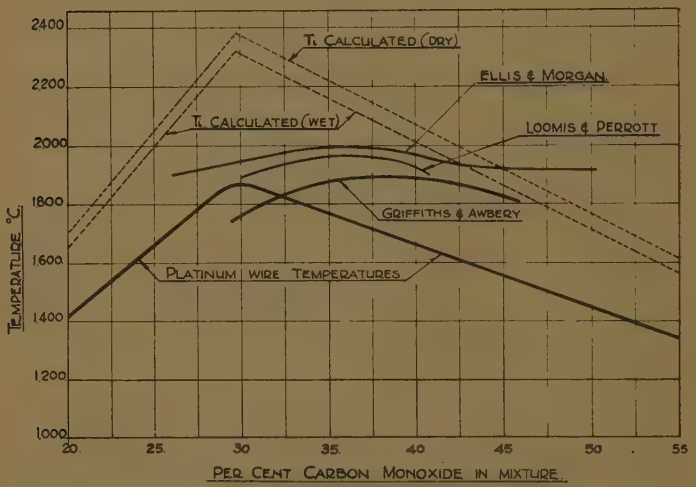



The steady platinum temperatures * and the sodium temperatures by Ellis and Morgan †, Loomis and Perrott‡, and Griffiths and Awbery § for CO–air mixtures of various strengths are shown in fig. 3. The sodium measurements by Ellis and Morgan and those by Loomis and Perrott were made in the immediate neighbourhood of the inner cone. Those by Griffiths and Awbery were made in the uniform region B′C′ (fig. 1), and these are, therefore. the sodium measurements which should be compared with the platinum measurements.

* Phil. Mag. xvii. p. 172 (1934).
† Trans. Faraday Soc. xxviii. p. 826 (1932).
‡ Ind. and Eng. Chem. p. 1007 (Oct. 1928).
§ Proc. Roy. Soc. A, lxxiii. p. 401 (1929).

Allowing for the fact that the sodium measurements were made with flames resulting from the combustion of water-vapour saturated CO–air mixtures, and that the platinum measurements were made with flames from relatively dry CO–air mixtures, it will be seen that in the neighbourhood of the " correct " CO–air mixture the Griffiths and Awbery sodium temperatures and the platinum temperatures correspond closely. As the CO–air mixtures become richer, however, there is an increasing difference between them—amounting eventually to some

Fig. 3.




Flame temperatures in carbon monoxide–air mixtures. The calculated temperatures are shown uncorrected for dissociation. As the actual temperatures in the flame gases are less than 2000°C., dissociation in them is small, and a fairer perspective is obtained by comparing them with calculated temperatures uncorrected for dissociation.

hundreds of degrees C. The sodium temperatures do not vary much with mixture strength (the sodium temperature for a 47 per cent. CO–air mixture—available oxygen 11·1 per cent.—is, for example, as high as, indeed even higher than, that for the " correct " mixture—available oxygen 14·8 per cent.), and this would seem at once to rule them out as measures of true temperatures. The

platinum temperatures, on the other hand, vary with mixture strength much in the manner to be expected from calculation; they drop by nearly 400° C. as the mixture strength is varied from the "correct" to 47 per cent. CO. Furthermore, if the sodium temperatures are brought under close examination it will be seen that the peak temperature occurs with a 38 per cent. CO–air mixture, and this by the method of Fenning and Tizard * suggests a dissociation of $CO_2$ in the flame from a "correct" mixture of the order of 20 per cent., whereas the dissociation at the temperature obtaining in the flame (under 1900° C.) must be small. The platinum temperatures show a peak value at or near the "correct" mixture, indicating small dissociation.

The sodium measurements of Griffiths and Awbery were very carefully made and the conclusion seems irresistible that sodium in flame gases does not provide a means of obtaining true temperatures.

The platinum method, as has been stated, yields temperatures which may be rationally correlated with mixture strength, but as will be seen from a comparison of the platinum and the calculated temperature curves, they are many hundreds of degrees below the calculated temperatures. The question therefore arises as to whether the platinum temperatures are too low. In this connexion it should be borne in mind that in flames resulting from the combustion of the correct mixture, in which radiation loss from the platinum wire and conduction into the platinum wire leads is greatest, the platinum temperatures correspond closely to the sodium temperatures, and it is highly probable that the sodium temperatures are too low. Indeed, it is only by assuming that the sodium temperatures are generally too high (especially with over-rich mixtures), in which case excess CO is present in the flames) that any interpretation of them would appear to be possible, and it is interesting to recall that Kohn †, measuring flame temperatures by the sodium method, first when an electrically heated platinum wire was placed in the flame and then with the platinum wire removed, found a higher temperature in the latter case.

Low as the platinum temperatures are in relation to the calculated temperatures, it is probable that they are

* Proc. Roy. Soc. A, cxv. p. 318 (1927).
† *Ann. Phys.* xliv. p. 749 (1914).

over-estimates of the true temperatures. Flame gases contain metastable molecules of some kind or other in considerable quantities, and these unload their energy when they strike the surface of the wire. In the case of flames resulting from the combustion of very weak and very over-rich mixtures there seems little doubt that the platinum wire temperatures are very much above the true flame temperatures. In such flames there is incomplete combination *, resulting in surface combustion on the wire. It will be recalled in this connexion that Davies † has shown that even a small amount of uncombined gas will affect the platinum wire temperature very considerably, and, indeed, in some of our experiments with flames from very weak hydrogen mixtures the platinum wire temperatures were much above the ideal calculated temperatures †.

Estimates which we have made of the latent energy in flame gases (some of which we have published ‡) are based on the assumption that the platinum wire gives true temperatures, and it will be clear from what has been said above that I believe them to be under-estimates rather than over-estimates—particularly in the case of very weak and very over-rich mixtures.

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XXVI. *The Influence of Magnetic Field on Adsorption.* *By* Prof. S. S. Bhatnagar, O.B.E., D.Sc., P. L. Kapur, *M.Sc., and* A. N. Kapur, *M.Sc.* §.

THE effect of magnetic field on the rate of crystallization, viscosity, dielectric constant, electrical resistance, and fluorescence is well known. The close interdependence of electrical, magnetic, and chemical forces leads one to expect that magnetic field would influence the course of a chemical reaction. The earlier work on the subject presents a lot of conflicting evidence and has

* 'Gaseous Combustion at High Pressure', Bone, Newitt & Townend (Longmans, Green & Co., 1929), pp. 313 *et seq.*

† Phil. Mag. xvii. p. 233 (1934).

‡ Proc. South Wales Inst. Engineers, 1936, p. 375, and Phil. Mag. xxi. p. 280 (1936).

§ Communicated by the Authors.

been critically examined by Bhatnagar, Mathur, and Kapur [1]. From the results obtainable then they concluded that a reaction would be accelerated, retarded, or remain unaffected according to whether the sum of the molecular susceptibilities of the products is more, less, or equal to the sum of the molecular susceptibilities of initial substances. These views were later confirmed by Rozenberg and Yuza [2], who showed that the rate of dissolution of ferro- and paramagnetic metals in acids in magnetic field is retarded, while that of diamagnetic metals in acids is augmented. Similar observations have also been made by Forrestier [3], who has studied the effect of magnetic field on the electrolysis of different salts and on the corrosion of iron by salts of different noble metals.

We have been interested in these laboratories for some years in investigating the effect of magnetic field on adsorption. The earliest efforts were those of one of us with Messrs. S. D. Mahant and B. S. Gupta [4], when an attempt was made to study the changes in adsorption by colloidal solutions, and these results are being communicated separately.

In this investigation the adsorption in the following systems has been studied in and outside the magnetic field :—

Adsorption of $KMnO_4$ by charcoal.
,, $K_2Cr_2O_7$ ,,
,, $FeCl_3$ ,,
,, $K_4FeCy_6$ ,,
,, $KMnO_4$ by $BaSO_4$
,, $K_4FeCy_6$ ,,

## Experimental.

The adsorption experiments were performed in two exactly similar tubes, 30 cm. long and 1·5 cm. wide, with a side-tube in the centre for the thermometer. These tubes could be placed in the field of a powerful electromagnet on rests fixed to the ends of the pole-pieces. The pole-pieces were plane-parallel and 28 cm. long. With a current of 8 amps. a field of 15,000 gauss was obtained in a gap of 2 cm.

The chemicals employed were all Merck's extra pure reagents. The adsorbent carbon was supplied to us by

Dr. K. G. Mathur, Emerson Fellow of the Punjab University, to whom our thanks are due. It was again washed with water and reheated to 850° C. *in vacuo*. The adsorbent carbon thus obtained was ground to a fine powder in an agate mortar and passed through a 90-mesh sieve.

Equal amounts of the adsorbent were carefully weighed and transferred into the tubes. The tubes were placed one inside and the other outside the field. Equal volumes of the solution were pipetted in each tube. The tubes

## Results.

### Table I.

Adsorption of $KMnO_4$ on Sugar Charcoal. Temperature 25° C. Amount of Adsorbent 0·5 gm.

| Amount of $KMnO_4$ before adsorption. | $KMnO_4$ adsorbed. | | Change in amount of adsorption. due to magnetic field. | Remarks. |
|---|---|---|---|---|
| | Outside the field. | Inside the field. | | |
| gm. | gm. | gm. | gm. | |
| 1·525 | 0·785 | 0·819 | 0·0340 | There is definitely an increase in adsorption in the magnetic field. |
| 1·335 | 0·740 | 0·7724 | 0·0324 | |
| 1·026 | 0·654 | 0·6825 | 0·0285 | |
| 0·735 | 0·547 | 0·5710 | 0·0240 | |
| 0·605 | 0·480 | 0·5010 | 0·0210 | |

were tilted an equal number of times, and were allowed to remain for 45 minutes, after which the solutions were filtered through glass-wool and the amounts adsorbed estimated. All possible care was taken to keep the conditions of both sets of experiments, one in the magnetic field and the other outside, as identical as possible. The temperature of the solutions both inside and outside the field was noted during the course of the experiment, and was found not to vary by more than 0·2° C., the solution inside the field showing a slightly higher temperature.

There are three other factors besides the magnetic field which may influence adsorption, namely, variations in temperature, surface of the tubes, and unequal stirring. Blank experiments were performed outside the magnetic field to find how far the change in adsorption due to magnetic field could be ascribed to these causes. It was found that there was no change in the amount of

TABLE II.

Amount of Adsorbent —0·5 gm.

| Amount of $KMnO_4$ before adsorption. | Amount of $KMnO_4$ adsorbed at 25° C. | Amount of $KMnO_4$ adsorbed at 27° C. |
|---|---|---|
| 1·580 | 1·2450 | 1·2448 |
| 1·264 | 0·9052 | 0·9051 |
| 0·948 | 0·5979 | 0·5979 |

TABLE III.

Amount of Adsorbent 0·5 gm.

Temperature 25° C.

| Amount of substance before adsorption. | Amount of substance adsorbed. | | Change in amount of adsorption due to magnetic field. | Remarks. |
|---|---|---|---|---|
| | Outside the field. | Inside the field. | | |
| System.—Adsorption of potassium dichromate on sugar charcoal. | | | | |
| gm. | gm. | gm. | gm. | |
| 0·1849 | 0·0491 | 0·0532 | 0·0041 | Increased adsorption in the magnetic field. |
| 0·1629 | 0·0354 | 0·0384 | 0·0030 | |
| 0·1455 | 0·0260 | 0·0282 | 0·0022 | |
| System.—Ferric chloride on sugar charcoal. | | | | |
| 1·290 | 0·1300 | 0·1276 | 0·0024 | Decreased adsorption in the magnetic field. |
| 1·120 | 0·1250 | 0·1227 | 0·0023 | |
| 0·812 | 0·1120 | 0·1099 | 0·0021 | |
| System.—Potassium permanganate on barium sulphate. | | | | |
| 0·1264 | 0·0134 | 0·0135 | 0·0001 | No effect of magnetic field. |
| 0·1024 | 0·0121 | 0·0121 | 0·0000 | |
| 0·0810 | 0·0101 | 0·0100 | 0·0001 | |
| System.—Potassium ferrocyanide on barium sulphate. | | | | |
| 1·472 | 0·0281 | 0·0281 | 0·0000 | No effect of magnetic field. |
| 1·410 | 0·0240 | 0·0240 | 0·0000 | |
| 1·360 | 0·0160 | 0·0161 | 0·0001 | |
| System.—Potassium ferrocyanide on sugar charcoal. | | | | |
| 1·796 | 0·5668 | 0·6000 | 0·0332 | Increased adsorption in the magnetic field. |
| 3·2012 | 0·8012 | 0·8574 | 0·0562 | |

adsorption by interchanging the tubes. No stirring was done in both the tubes during the period the field was on. As is seen from Table II., variation in temperature even by 2° did not appreciably affect the amount of adsorption. Further, the rise in temperature, if at all,

decreases the adsorption, and this factor would work in opposite direction to the magnetic field. Thus it shows that the increased adsorption due to magnetic field is quite genuine and not due to any extraneous causes.

In the last system the filtrate was found to be more highly coloured than the original solution, possibly due to some potassium ferrocyanide having been oxidized to potassium ferricyanide. A second experiment was therefore performed, and the amount of potassium ferrocyanide converted into potassium ferricyanide was estimated iodometrically. The amount of potassium ferrocyanide oxidized to potassium ferricyanide outside the field was found to be 0·7968, while that inside the field was 0·8520 gm. Thus the amount of potassium ferrocyanide adsorbed outside the field was 0·0044 gm. and that inside the field was 0·0054 gm. This gave an increase in adsorption due to magnetic field of 0·0010 gm. Incidentally it might be pointed out that 0·0552 gm. more of potassium ferrocyanide was oxidized to potassium ferricyanide in the magnetic field.

## Summary and Discussion.

The results obtained can be summarized as below :—

| System. | Result. |
|---|---|
| $KMnO_4$ by charcoal .... | Increased adsorption in magnetic field. |
| $K_2Cr_2O_7$ ,, .... | ,, ,, ,, ,, |
| $FeCl_3$ ,, .... | Decreased adsorption in magnetic field. |
| $K_4FeCy_6$ ,, .... | Slight increase in adsorption in field, but $K_4FeCy_6 \rightarrow K_3FeCy_6$. |
| $KMnO_4$ by $BaSO_4$ .... | No effect of magnetic field. |
| $K_4FeCy_6$ by $BaSO_4$ .... | ,, ,, ,, |

Adsorption is rather a complex phenomenon. According to Langmuir [5] adsorption is due to surface forces. He states that the atoms in a solid (adsorbent) are held in the space lattice by attractive forces between the neighbouring atoms. At the surface, however, they are only held on one side, and so there will be a certain amount of latent surface energy which is accumulated around certain centres on the solid surface. These centres have definite relationship to the crystal lattice of the adsorbent, and the molecules adsorbed are held at these points by the residual affinity. Debye and Scherrer [6], from an X-ray study of activated carbon, concluded that it was the graphite in amorphous carbon which was responsible for adsorption; but this view was criticized by Ruff, Schmidt,

and Olbrich [7], who concluded that there were active centres of adsorption in amorphous carbon itself.

In 1930 Schilov [8], while studying the adsorption of acids by charcoal, observed that there was always a film of active oxide on the surface of carbon which could not be removed even on prolonged heating in a vacuum. He therefore suggested that adsorption was due to the interaction of ions adsorbed and surface oxides. This hypothesis has recently been supported by Lepin and Strachoiva [9]. Burrage [10] believes that the polar molecules only are capable of collecting round the active surface areas in active carbon. In the case of apolar molecules, he believes, polarity is induced. He further believes that $O_2$ and C form on the surface a spongy complex $C_xO_y$, which is responsible for adsorption. He observed that in the case of sorption vapours, such as water, broke up $C_xO_y$ and removed it as $CO_2$ at a slow rate, whereas others, such as $CCl_4$, removed it fairly rapidly.

In the system $KMnO_4$-charcoal filtrate after adsorption was found to contain a brown suspension which on analysis was shown to be $MnO_2$. The formation of $MnO_2$ during adsorption can be explained by assuming that while removing the complex $C_xO_y$ or on account of the interaction of C oxides $MnO'_4$ ion has been reduced to $MnO_2$. Formation of $Cr'''$ ion in the system $K_2Cr_2O_7$-charcoal after adsorption can be explained on similar lines. In the adsorption of $FeCl_3$ by charcoal the complex $C_xO_y$ probably forms carbonyl of iron, as suggested by Bhatnagar, Mathur, and Kapur [11], and is thus removed. In the adsorption of $K_4FeCy_6$ by charcoal after adsorption part of $K_4FeCy_6$ was found oxidized to $K_3FeCy_6$. This can be explained by assuming that the complex $C_xO_y$ here acts as an oxidizing agent. Thus the complex is not only capable of reducing the adsorbate, as in the case of adsorption of water vapour, $CCl_4$ vapour and $KMnO_4$ solution, but it may combine and form a new compound as in the case of adsorption of $FeCl_3$, or, lastly, it may oxidize the adsorbate as in the case of $K_4FeCy_6$. The behaviour of the complex depends on the nature of the adsorbate. These observations are in line with those of other workers [12] and support the chemical theory of adsorption.

Now, since adsorption has been shown to be chemical

in nature, the magnetic field should influence it in accordance with the rules formulated by Bhatnagar, Mathur, and Kapur (*loc. cit.*), *i. e.*, if

$$\Sigma_f \chi_M > \Sigma_i \chi_M$$

the amount adsorbed would be more in the magnetic field, if

$$\Sigma_f \chi_M < \Sigma_i \chi_M$$

the amount adsorbed would be less, and if $\Sigma_f \chi_M = \Sigma_{\chi_i M}$ the field would have no influence, where $\Sigma_f \chi_M$ = sum of the molecular susceptibilities of the final products and $\Sigma_i \chi_M$ = sum of the molecular susceptibilities of initial reactants. These rules can be applied quantitatively only if the $\chi_M$ of initial and final products are accurately known. In adsorption the reactants are adsorbate and the complex $C_xO_y$ in cases where charcoal is adsorbent, and in other cases the adsorbent itself. The $\chi_M$ value of all the components of adsorption cannot be accurately determined, because neither do we know the composition of complex $C_xO_y$ nor the exact state of the adsorbate after adsorption. However, since adsorption is due to a state of unsaturation in the adsorbent, the suboxide $C_xO_y$ would be paramagnetic, on adsorption the adsorbed molecules will attach themselves to the complex $C_xO_y$ by the residual affinities of the carbon atom, and the product formed may be more or less paramagnetic than originally. Actually it was found that pull per gram on a Gouy balance for charcoal before and after adsorption of $KMnO_4$ was 0·163 gm. and 0·182 gm. respectively. It is clear, therefore, that in this case $\Sigma_f \chi_M$ will be greater than $\Sigma \chi_M$ even if we suppose that the susceptibility of the complex $C_xO_y$ does change after adsorption. Taking the $\chi_M$ value of other components, then we can tabulate the results as follows :—

| Systems. | | $\Sigma_i \chi_m$. | $\Sigma_f \chi_M$. | Change in adsorption. |
|---|---|---|---|---|
| I. $KMnO_4$ $C_xO_y$ | $= MnO_2$ $(C_nO_m)$ | 27·825 | 3340·8 | Increased. |
| 27·825 | 3340·8 | | | |
| II. $K_2Cr_2O_7$ $C_xO_y$ | $= Cr_2O_3$ $(C_nO_m)$ | 37·93 | 3876·0 | ,, |
| 37·93 | 3876 | | | |
| III. $FeCl_3$ $C_xO_y$ | $= Fe(CO)_5$ | 14007·5 | −78·4 | Decreased. |
| 14007·5 | −78·45 | | | |
| IV. $K_4FeCy_6$ $C_xO_y$ | $= K_3FeCy_6$ | 134·688 | 2293·13 | Slight increase. |
| 134·688 | 2293·13 | | | |
| V. $BaSO_4$ $KMnO_4$ | $= BaSO_4 - KMnO_4$ | −43·473 | −43·473 | No effect. |
| −71·298 27·825 | −71·298 27·825 | | | |
| VI. $BaSO_4$ $K_4FeCy_6$ | $= BaSO_4 - K_4FeCy_6$ | | | |
| −71·298 134·688 | − 71·298 134·688 | 63·390 | 63·390 | No effect. |

From the above table it is clear that when $\Sigma_f \chi_M > \Sigma_i \chi_M$, as in the systems I., II., and IV., there is an increase in adsorption in the magnetic field; in system III., where $\Sigma_f \chi^M < \Sigma_i \chi_M$, there is decrease in adsorption, and in systems V. and VI., where $\Sigma_f \chi_M$ is nearly equal to $\Sigma_i \chi_M$, there is no influence of magnetic field. Thus we find that the results obtained by us are in line with those obtained by Bhatnagar, Mathur, and Kapur (*loc. cit.*).

If the view that as a result of adsorption of $KMnO_4$ by charcoal $MnO_2$ is formed be correct, then, because magnetic field increases the amount of $KMnO_4$ adsorbed, more of $MnO_2$ should be formed by adsorption inside the field than outside. No chemical method could be employed because of the difficulty of removing $MnO_2$ and $MnO'_4$ from charcoal; therefore we had to resort to a magnetic method. Pull per gram of the two samples was determined on a Gouy balance set in this laboratory. It was found that the pull per gram of the charcoal which had adsorbed $KMnO_4$ in the field was equal to 0·207 gm., and that due to the one which had adsorbed $KMnO_4$ outside the field was equal to 0·182 gm. This clearly shows that inside the field more of $MnO_2$ was formed during the adsorption of $KMnO_4$ by charcoal, and thus confirms the view that $MnO'_4$ is reduced by $C_xO_y$ complex to $MnO_2$.

Thus we find that magnetic field influences adsorption as it does various other chemical reactions according to rules deduced by Bhatnagar, Mathur, and Kapur (*loc. cit.*).

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## XXVII. *Absorption of Infra-red Light in Supraconductors.*

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### *Introduction.*

VERY little is known about the optical properties of supraconductors, and so far only the photo-electric effect of lead and mercury was investigated by McLennan, Hunter, and McLeod [1]. No appreciable change, however, was observed when the metal passed from the normal into the supraconductive state.

Of the other optical properties reflexion seems to be of particular interest. Drude has connected electric conductivity and reflexion of a metal by a simple formula. According to his equation the reflexion of a metal of which the electric resistance becomes zero should be 100 per cent. The validity of the formula is limited, as it cannot be applied in the visible or ultraviolet. Hagen and Rubens have shown, however, that it holds in the infra-red.

Although Drude's formula has to be considered as a first approximation to the description of the actual relationship between optical and electrical properties of a metal, it is evident from the experimental results that the same processes are responsible for the electric resistance and the absorption of light. As at the transition from the normal to the supraconductive state the resistance of the metal vanishes entirely a change in the optical absorption could also be expected, and experiments of this kind might give us direct evidence of the behaviour of supraconductive electrons. Experiments on the reflexion of Sn, Pb, Hg, NiC, and $PbTl_2$ in the near infra-red and in the visible were carried out by one of us in collaboration

* Communicated by the Authors.

with R. Suhrmann [2] in 1932. In these investigations the reflected light was measured with a photocell. No change of reflexion could be observed when the metal became supraconductive. As, however, the reflexion is already very near to 100 per cent. in pure metals in the normal state, owing to their high conductivity, and as it has been shown by Keeley and Mendelssohn [3] and Mendelssohn and Moore [4] that supraconductive alloys behave anomalously in various respects, the results could not be considered very conclusive. It was therefore determined to repeat the experiment in the farther infra-red and by direct determination of the absorption. Apart from the fact that in this case the observed effect will be of a much greater order this method has the advantage that the metal surface has not to be polished and that errors arising out of a distortion of the lattice by the polishing of the metal are avoided.

## *Method.*

For the experiments an isothermal calorimeter was employed. As the sample the absorption of which was determined had to be cooled down to a very low temperature in order to make it supraconductive the advantages of a calorimetric method are obvious ; for owing to the smallness of heat capacities and latent heats in this temperature region, the good thermal insulation, and the absence of stray radiation even very small thermal energies can be determined with high accuracy. For an isothermal method the use of an evaporation calorimeter suggests itself. The only liquid available in this region is helium, which has a heat of evaporation of 5·5 cal./g., which means that ·001 cal. evaporate a volume of about 1 c.c. helium gas under normal conditions.

We used a small helium liquefier working on the expansion method [5]. This had the advantage that the expansion chamber in which the helium was liquefied could also be used as the helium container of the calorimeter.

A diagrammatical sketch of the whole arrangement is given in the figure. A is a strong-walled copper container in which the helium is liquefied. It is suspended by three German-silver wires $w$ in a thin-walled metal chamber B, which can be evacuated through the tube $T_1$. In order

to diminish the heat-conduction from the outside to A a large number of turns of the thick-walled German-silver tube $T_2$ are enclosed in the vacuum chamber. On top of A the supraconductive specimen C is mounted. At the lower end of $T_1$ a shutter D is mounted, which can be worked by the cord E, the upper end of which is connected to a small iron cylinder F in the evacuated glass tube G. By moving F with the aid of a small magnet H outside the glass tube the shutter can be opened and closed. The vacuum chamber is immersed in a bath of liquid hydrogen, the temperature of which can be reduced by pumping off through the tube $T_3$. In order to avoid secondary radiation the inside of the vacuum chamber B is blackened.

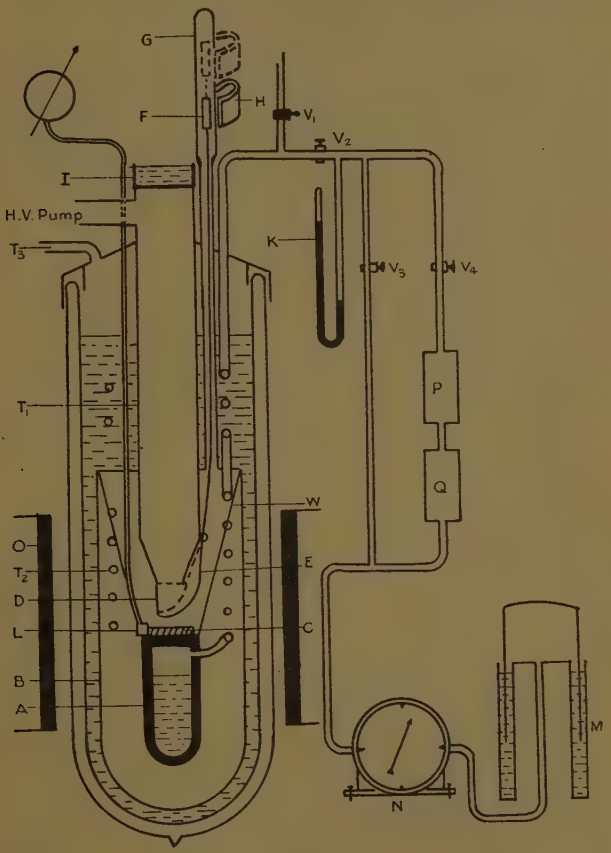
For the infra-red radiation we used thermal radiation of room-temperature which has a flat maximum at about $10\,\mu$. The source was a strong-walled copper pot I on top of $T_1$, which was filled with water. The outer side of the bottom of I facing C was blackened.

The specimens C were prepared in the following way :— (1) Tin " Analar " (Hopkin and Williams) was melted in a crucible and poured into a flat copper pan, so that the meniscus with an oxide layer stood a little above the rim of the pan. Then a flat disk of carbon was slid over the pan, thus pushing away the oxide and the upper layer of the liquid. After the whole pan had been covered the tin was allowed to cool. When the carbon was taken away after the solidification of tin the surface obtained was clean and showed some large crystals. (2) Lead " Analar " (Hopkin & Williams): the same procedure employed by the production of the tin specimen was also tried with lead. The surface, however, oxidized immediately after preparation before it could be protected. After pouring the lead into the pan therefore the specimen was brought, still liquid, into a $CO_2$ atmosphere, when the oxide layer was taken off and the sample allowed to cool. Finally, the surface was protected against oxidation by a very thin layer of varnish transparent in the infra-red.

The pans with the specimens were fixed to the upper part of the helium container A with Wood's alloy.

The temperature was determined from the vapour pressure of the liquid helium in A by the manometer K and by a simple gas thermometer L [6] which was attached next to the specimen.

The experiments were carried out in the following way :—At first helium was compressed into the chamber through the valve $V_1$. The heat of compression was




carried away to the hydrogen bath by a little helium gas in B. At the same time the temperature of the hydrogen-bath was decreased by pumping off to about 14° K. After A had been filled with compressed helium $V_1$ was closed, B exhausted, and the helium was allowed to expand through $V_2$ and $V_3$ into the gasometer M. Equilibrium

was finally attained when the liquid helium which had formed in A evaporated under atmospheric pressure (4·2° K., the actual pressure was a little higher owing to the weight of the gasometer dome, and corresponded to 4·22° K.).

The rate of evaporation which was now observed corresponded to the heat carried from the outside to A as well by conduction through the wires *w* and the tube $T_2$ as by radiation from B. The evaporating gas was measured by a gas-meter N and controlled by a flow-meter (not shown in the diagram). Now the shutter D was opened, radiation from the source fell on the specimen, and by the energy absorbed the rate of evaporation was increased. Finally, a magnetic field was established with the solenoid O, and supraconductivity destroyed, and again the evaporation measured at the same temperature.

In the case of tin, which has a transition point at 3·7° K., it was necessary to determine the evaporation at a reduced vapour pressure of the helium. For this purpose $V_3$ was closed and $V_4$ opened, and the helium passed into a pressure regulator P and a pump Q before it entered the gas-meter. The pressure regulator was the same as has been described by one of us [7], and kept the temperature constant to 0·003° K.

In order to ensure reproducible conditions the hydrogen in the bath was allowed to warm up to 20° K. immediately after the expansion, and its meniscus was always kept at the same height well above the vacuum space B.

*Results.*

Neither on lead nor on tin could a change in the absorption be observed when the metal was transformed from the supraconductive into the normal state by the application of a magnetic field.

For the accuracy of the experiment it is essential that evaporation caused by the absorption of light from the source is of the same order as or larger than the evaporation with closed shutter. This condition was certainly fulfilled in all our experiments; and in the case of lead investigated at 4·22° K. the evaporation due to absorption from the source was more than twice as big as with closed shutter. In our measurements we determined the time which was needed for the evaporation of a certain

amount of the gas (usually 1·42 c.c.). These values varied by $\pm 3$ per cent., which means that the absorption determined was accurate to $\pm 5$ per cent. In the table the total evaporation with shutter closed and open as well as the evaporation due to the absorption from the source only are given. It can be seen that the absorption in the non-supraconductive state is slightly less than that of the supraconductive. The difference, however, is smaller than the limits of our accuracy. Similar results were obtained on tin. Owing to a much higher variation of the values of evaporation obtained the results for the absorption were less accurate ($\pm 15$ per cent.).

Lead at 4·22° K.

| | Evaporation c.c./min. |
|---|---|
| Total evaporation at closed shutter (no radiation) | 11·3 $\pm$ 3% |
| „ „ open „ (field zero) | 41·5 $\pm$ 3% |
| „ „ „ „ (field 700 Gauss) | 40·0 $\pm$ 3% |
| Evaporation due to absorption on supraconductive surface | 30·2 $\pm$ 5% |
| „ „ „ non-supraconductive surface | 28·7 $\pm$ 5% |

*Discussion.*

It is evident from the result of the investigation that the energy exchange between electrons accelerated by a light wave and the crystal lattice is approximately the same in the normal and in the supraconductive state. Accordingly, two possibilities of explanation suggest themselves :—(*a*) that the number of supraconductive electrons is so small that they do not contribute appreciably to the optical absorption, or (*b*) that if the number of supraconductive electrons is of the same order as that of the ions the individual electrons cannot be absolutely free.

(*a*) An indication that the number of supraconductive electrons is zero at the normal transition point and increases with decreasing temperature is given by the experiments of de Haas and Bremmer [8] on the thermal resistance of a supraconductor *.

* It is obvious, however, that this is not the only way by which the experiments of de Haas and Bremmer could be explained, and that they do not necessarily contradict the assumption that all electrons pass into the supraconductive state.

De L. Kronig [9] has recently pointed out that the change in thermal conductivity occuring when a metal is transformed from the normal to the supraconductive state below the transition temperature by applying a magnetic field should be identified with the fraction of ordinary conducting electrons entering the supraconductive state. These electrons are supposed to be "entirely free." Therefore he expects a change in the reflexion coefficient if the change in thermal conductivity is big enough. In the case of lead at 4·2° K., where our experiments are most accurate, this change amounts according to the experiments by de Haas and Bremmer to approximately 30 per cent. No change of this order, however, was observed in the absorption.

(*b*) Experiments on the energy content of supraconductors, on the contrary, seem to suggest that at the transition point not only a fraction but all free electrons pass into a new state. If the individual supraconductive electrons were entirely free the absorption should be zero, as no interaction with the lattice exists. In regard to our experiment this possibility must be excluded. We know, on the other hand, that in the supraconductive state electrons can move through the metal without the development of Joule heat. A possible explanation therefore is that the macroscopic supra-currents which we observe in conductivity experiments are due to an organized movement of all or at least very many electrons, and that during a light vibration there is not sufficient time to start such an organized movement *.

Summing up these considerations the outcome of our experiments seems to indicate that either the number of supraconducting electrons is very small, *i. e.*, much smaller than would be expected from the change in heat conductivity, or, what seems more probable, that all electrons pass into the supraconductive state but are by no means entirely free. In this case we are led to the assumption that the free movement of electrons in the supraconductive state must be a collective phenomenon.

In order to investigate the first possibility more accurate experiments would have to be carried out, so as to find out whether a small change in the absorption occurs

* We are much indebted to Dr. R. Peierls for discussions on these questions.

and whether that change varies with temperature. Evidence for the second explanation can be found by experiments with lower frequencies. In such an investigation a wave-length should be found at which the collective movement of the electrons begins to follow the accelerating wave. Experiments of this kind are under way in this laboratory.

Our thanks are due to Professor F. A. Lindemann, F.R.S., for putting the facilities of the laboratory at our disposal and for his kind interest in this research, and to Imperial Chemical Industries, Ltd., for making this work possible for one of us.

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September 8th, 1936.

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## XXVIII. *The Dynamical Theory of Electron Diffraction and its Application to some Surface Problems.* *By* J. W. Harding, *M.Sc., Ph.D., Imperial College of Science and Technology, London* *.

### *Introduction.*

BETHE has given a dynamical theory of electron diffraction [1] which is very similar in its scope and general predictions to the dynamical theories of X-ray diffraction which were developed much earlier by Darwin [2] and by Ewald [3].

The fundamental problem of all these theories is to calculate the intensity of the beam reflected from a given

* Communicated by Prof. A. O. Rankine, F.R.S.

family of planes in the crystal, and to predict the variation of the intensity of reflexion with the angle of incidence and the wave-length of the incident (monochromatic) beam. In the true "reflexion" case when the beam after reflexion emerges on the same side of the crystal surface as the incident beam, the dynamical theories of Darwin and of Ewald for X-rays and of Bethe for electrons all predict that over a certain range of wave-length or a certain range of angle of incidence the incident beam will be totally reflected by the crystal planes, and that the wave in the crystal will suffer "dynamical extinction" over this range, the extinction being due solely to the interaction of the waves which are scattered inside the crystal and not to any true absorption in the crystal.

In the case of X-rays the predictions of the theory have been very satisfactorily verified by experiment; but this is not by any means the case with the corresponding electron theory.

Laue has criticized Bethe's treatment of the boundary problem on the grounds that electrostatic theory demands that there must be a modification near the boundary of the potential proper to the interior of the crystal, and that, in consequence, it is not legitimate to terminate in an arbitrary fashion at the boundary the triply periodic potential which is assumed for the interior as Bethe has done in his theory. Laue reaches no very definite conclusions as to the error involved in Bethe's treatment; but estimates that the error is probably small provided that the incident electrons have a velocity greater than that corresponding to about two hundred volts.

Experiments carried out with electrons of velocities well above two hundred volts show, however, a serious discrepancy between the observed breadth of selective (or total) reflexion and that predicted by the Bethe theory. Several years ago, in the course of some observations which were made on the intensity of an electron beam reflected from the planes parallel to a (111) natural face of diamond, G. P. Thomson found that the reflected spot was visible on the screen almost all the time while the crystal was rotated steadily so as to give reflexions in successive orders. More recent quantitative measurements of the intensity variation [4] show, for example, that with forty thousand volt electrons the half-intensity breadth is about thirty minutes for the third order

reflexion, while a calculation of the theoretical breadth gives about two minutes.

Unfortunately there appear to be no reliable observations for the intensity distribution from a metal crystal owing to the great difficulty which is experienced in obtaining a good cleavage surface in this case. The diffraction patterns which are obtained by "reflexion" from metals are usually transmission patterns obtained by etching the surface, in which case the electron beam passes through the ridges on the surface which are produced by the etching process.

However, the effect has been observed in certain other crystals which give good cleavage or natural faces, and recently Kikuchi [5] has found that for zinc blende the reflexion region is about twenty times that predicted by the theory, which is in general agreement with Beeching's results for diamond.

The theory of Bethe stresses the analogies which exist between the diffraction of electrons and that of X-rays; but it must be remembered that there are very important quantitative differences, the chief of which is the large interaction between the electron beam and the scattering crystal compared with the case of X-ray scattering. With the latter the penetration of the beam is so great that the contribution of the planes near the surface to the diffracted beam is relatively insignificant, so that a correct treatment of the boundary problem, which is difficult, is not of very great consequence. This is not the case with high velocity electrons where the glancing angle of diffraction is small and of the order of a few degrees, and where, in consequence, the electrons have to encounter many more atoms before reaching a given depth from the surface than they would have to at larger angles of diffraction. It is very difficult to determine the effective penetration at these small glancing angles; but a combination of theoretical and experimental data suggests that it may not be more than about ten planes, and possibly less. It is clear that it is not legitimate under these circumstances to leave true absorption out of account as in the Bethe theory, and that it is necessary to take into consideration any possible alteration in the structure of the upper planes, since even one or two planes may contribute appreciably to the pattern. This is, of course, why electron diffraction with high velocity

electrons is such a valuable instrument of research in all problems relating to surface structure ; but it is just this feature which considerably complicates the mathematical problem, and in order to make any progress one has to use a comparatively crude model.

The introduction of absorption alone is not sufficient to explain the experimental results, since absorption actually decreases the breadth of the region of selective reflexion. To account for the results it has been found necessary to assume that a few of the crystal planes near the surface act in the diffraction process as a unit which is partly independent of the main body of the crystal. This may happen in at least two ways.

(*a*) The theory of crystal cohesion [6] predicts a contraction of the crystal spacing near the surface, and the diffraction of the incident beam by these distorted planes may give rise to a diffracted beam which is partly out of phase with the main diffracted beam from the interior of the crystal.

(*b*) A similar effect may be produced by the presence of layers of foreign material such as gas on the crystal surface.

In the first part of this paper we develop a theory of electron diffraction which is based on that of Darwin for X-ray diffraction. Darwin's treatment has been generalized to allow for an arbitrary arrangement of planes near the crystal surface, and some typical cases have been treated by this method. The second part is devoted to a discussion of the fundamental problem of the breadth of the region of selective reflexion.

## Part I.

### *Electron Diffraction Theory for Variable Plane Spacing.*

1. *The Problem.*—The problem to be considered is that of the diffraction of a beam of electrons by a series of atomic planes which are parallel to a natural or cleavage face of a crystal and which are arranged according to some prescribed law.

Let the origin of coordinates be taken in a surface atom, let the inward drawn normal to the crystal surface be taken as the $z$-axis, and let the grazing angle of incidence

be $\theta$. The potential energy of an electron in the direction normal to the surface may be represented by the Fourier series $V(z)$, and the wave equation of the problem is then

$$\Delta\Psi + \frac{8\pi^2 m}{h^2}[E - V(z)]\Psi = 0.$$

The solution must be of the form

$$\Psi = e^{i(K, R)}\psi(z),$$

where R is a vector in the crystal surface.

The equation for $\psi(z)$ is then

$$\frac{d^2\psi}{dz^2} + \left[K_z^2 - \frac{8\pi^2 m}{h^2}V(z)\right]\psi = 0,$$

where we have put

$$\frac{8\pi^2 m}{h^2}E = |K|^2 = k^2 = K_x^2 + K_y^2 + K_z^2.$$

This equation is a Hill's equation, and the established theory of this equation has been applied to the diffraction problem by Morse [7].

Instead of solving this differential equation, we may adopt the method which was employed so successfully by Darwin in the case of X-rays. In the particular and important case of a constant spacing of the planes this method enables a solution to be obtained in a very simple form, and the method can readily be extended so as to apply to a more general arrangement of planes. It is also easy to make some allowance for absorption, which is important in the case of electrons.

In Darwin's method one first calculates the reflexion coefficient of a single plane of atoms, and then one sets up a system of difference equations in order to take account of the interaction of the waves which are scattered inside the crystal.

This method of treating the electron diffraction problem will be seen to resemble that associated with the names of Kronig and Penney [8]; but the actual course of the calculations is different, since in our case the problem is made to depend on the solution of two or more simultaneous difference equations.

2. *Diffraction by a Single Plane of Atoms.*—We first consider the interaction between an incident electron

beam and a single plane of atoms, which we represent by a rectangular potential barrier of height $V_0$ and breadth $b$ (fig. 1).

The Schrödinger equation gives for the wave functions in the three regions (fig. 1)

$$\psi_1 = A_1 e^{i\alpha z} + A_2 e^{-i\alpha z}, \quad z<0,$$

$$\psi_2 = B_1 e^{\beta z} + B_2 e^{-\beta z}, \quad 0<z<b,$$

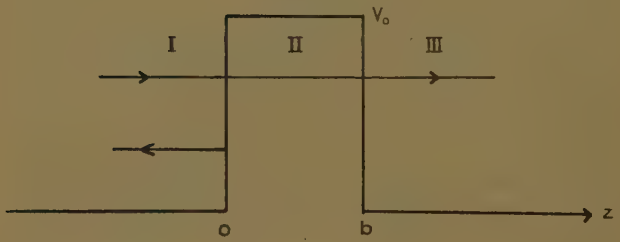
$$\psi_3 = C e^{i\alpha z}, \quad z>b,$$

where

$$\alpha^2 = \frac{8\pi^2 m}{h^2} E_z = K_z^2,$$

$$\beta^2 = \frac{8\pi^2 m}{h^2} (V_0 - E_z).$$

Fig. 1.




The amplitudes are determined by the usual boundary conditions, and a simple calculation yields

$$A_1 = \tfrac{1}{4} C e^{i\alpha b} \left[ 2(e^{\beta b} + e^{-\beta b}) + i \left( \frac{\beta^2 - \alpha^2}{\alpha\beta} \right) (e^{\beta b} - e^{-\beta b}) \right].$$

It is now supposed that the barrier becomes infinitely high, and that its breadth tends to zero in such a way that

$$\underset{\substack{b\to 0 \\ \beta\to\infty}}{\text{Lim.}} \frac{\beta^2 b}{2\alpha} = P.$$

This is the limiting process employed by Kronig and Penney, except that they use it at a later stage of the calculations ; it is the approximation which corresponds to the Darwin plane of atoms.

Proceeding to the limit we find that

$$D = \frac{C}{A_1} = \frac{1-iP}{1+P^2},$$

where $|D|^2$ is the transmission coefficient.

Similarly, we find

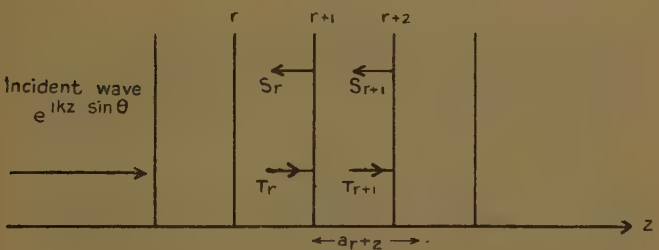
$$\frac{A_2}{A_1} = -\frac{(\beta^2+\alpha^2)(e^{\beta b}-e^{-\beta b})}{(\beta^2-\alpha^2)(e^{\beta b}-e^{-\beta b})-2i\alpha\beta(e^{\beta b}+e^{-\beta b})},$$

and in the limit

$$R = \frac{A_2}{A_1} = -\frac{P(P+i)}{1+P^2},$$

where $|R|^2$ is the reflexion coefficient.

Fig. 2.




3. *The Fundamental Difference Equations.*—We must now find the combined effect of a number of these planes when they are arranged according to an arbitrary law.

The normal component of the incident wave, which is the only part we are concerned with here, is represented by $e^{ikz\sin\theta}$. Following Darwin's treatment (*loc. cit.*) for X-rays, let $S_r$ and $T_r$ represent in amplitude and phase the total reflected and transmitted wave respectively when these are measured just above the $(r+1)$th plane, and let $a_{r+2}$ be the lattice spacing above the $(r+2)$nd plane, the quantity $a_{r+2}$ replacing Darwin's constant spacing $a$.

For the reflexion and transmission coefficients of a single plane we introduce the quantities R and D defined above, and we represent the true absorption in the plane by means of a coefficient $h$, which represents an absorption coefficient of approximately $2h$, since

$|R|^2+|D-h|^2+2h \doteq 1$. If we require the value of $S_{r+1}$ just below the $(r+1)$th plane instead of just above the $(r+2)$nd plane we must multiply by the factor $e^{+ika_{r+2}\sin\theta}$.

$S_r$ (see fig. 2) is then built up out of the part of $T_r$ reflected from the $(r+1)$th plane and the part of $S_{r+1}$ transmitted from the plane below, and so on, so that we find as the equations which represent the interaction between the S and T waves

$$S_r = RT_r+(D-h)S_{r+1}e^{ika_{r+2}\sin\theta}, \quad . \quad . \quad . \quad (1)$$

$$T_{r+1}e^{-ika_{r+2}\sin\theta} = (D-h)T_r+RS_{r+1}e^{ika_{r+2}\sin\theta}. \quad . \quad (2)$$

The elimination of $S_r$ yields the following equation for $T_r$:—

$$(D-h)T_{r+2}e^{-ik(a_{r+3}-a_{r+2})\sin\theta} + [R^2-(D-h)^2-e^{-2ika_{r+2}\sin\theta}]e^{ika_{r+2}\sin\theta}T_{r+1}+(D-h)T_r=0 \quad . \quad . \quad . \quad (3)$$

and a similar equation for $S_r$ on elimination of $T_r$.

These equations are the obvious generalization of Darwin's equations to include the case of an arbitrary arrangement of planes.

We shall now solve these equations in certain special cases.

4. *The Bethe Case.*—$h=0$ and $a_{r+2}=a$ (a constant).

In the neighbourhood of the Bragg angle, $\theta_B$, defined by the equation

$$n\pi = ka\sin\theta_B,$$

where $n$ is the order of the reflexion, we may write

$$ka\sin\theta = ka\sin(\theta_B+\tau) = n\pi+v,$$

$$e^{\pm ika\sin\theta} = (-)^n(1-iv-\tfrac{1}{2}v^2),$$

where $v=ka\tau\cos\theta_B$, and $\tau$ is the deviation from the Bragg angle.

Equation (3) then reduces to

$$T_{r+2}+(-)^n[v^2-2Pv-2]T_{r+1}+T_r = 0.$$

If we substitute

$$T_r = x^r,$$

we find that $x$ must satisfy the characteristic equation

$$x^2+(-)^n[v^2-2Pv-2]x+1 = 0,$$

which corresponds to the dispersion equation of the Ewald-Bethe theory.

The roots of this equation are nearly equal to unity, so we put

$$x = (-)^n(1-\epsilon),$$

and find

$$\epsilon = \pm i\sqrt{v(v-2\mathrm{P})} \quad \text{if } v>2\mathrm{P}.$$

The case $v<2\mathrm{P}$ will be discussed below.

The general solution is then, since $\epsilon$ is small, of the form

$$\mathrm{T}_r = (-)^{nr}\mathrm{T}_0^{(1)}e^{i\alpha r} + (-)^{nr}\mathrm{T}_0^{(2)}e^{-i\alpha r},$$

where $\alpha = \sqrt{v(v-2\mathrm{P})}$, and $\mathrm{T}_0^{(1)}$, $\mathrm{T}_0^{(2)}$ are arbitrary periodic coefficients of period unity.

For the amplitude of the reflected wave we must have

$$\mathrm{S}_r = (-)^{nr}\omega\mathrm{T}_0 e^{-\epsilon r},$$

and if this expression is substituted in the original equations (1) and (2) we find that the solutions for $\mathrm{T}_r$ and $\mathrm{S}_r$ are consistent if

$$\omega = \frac{\mathrm{S}_0}{\mathrm{T}_0} = \frac{\mathrm{P}}{v-\mathrm{P}\mp\alpha} = \frac{v-\mathrm{P}\pm\alpha}{\mathrm{P}} \quad . \quad . \quad . \quad . \quad (4)$$

*The Region of Total Reflexion.*

If $v$ is positive, that is, if $\tau$ is positive and $v<2\mathrm{P}$, one of the above solutions becomes infinite in the half-plane of the crystal when the crystal is taken to be infinitely thick, and consequently this solution must be rejected as a proper function of the problem. The other solution decreases exponentially from the surface and corresponds to the complete damping out of the crystal wave. If $\tau$ is negative, however, $\alpha$ is always real, and a transmitted wave is propagated through the crystal. We hence obtain total reflexion in the region $0<v<2\mathrm{P}$ if the crystal is sufficiently thick.

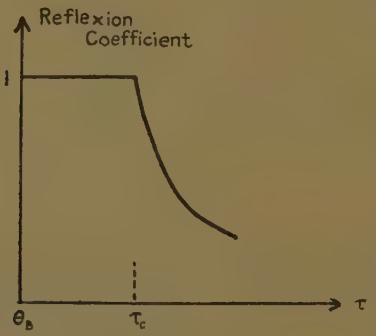
This differs in one respect from Darwin's result. If P is not too large, the value taken here for the ratio of the reflected to the incident amplitude for a single plane, namely, $\mathrm{R} = -\dfrac{\mathrm{P}(\mathrm{P}+i)}{1+\mathrm{P}^2}$, agrees formally with Darwin's expression $-iq$, so that one would expect to get identical results. However, Darwin finds for $\epsilon$ the expression

$\pm i\sqrt{v^2-q^2}$ instead of the above $\pm i\sqrt{v(v-2q)}$. Consequently Darwin obtains the same breadth for the region of selective reflexion as we do ; but his region of selective reflexion is symmetrical about the Bragg angle $\theta_B$, whereas ours (fig. 3) is displaced to larger angles.

*The Boundary Conditions.*

The solutions obtained for the interior of the crystal must now be fitted to the external solutions at the boundaries. We shall simplify the algebra by ignoring the refraction of the wave at the surface, since this does not materially affect the applications we have in view ;

Fig. 3.




and this omission can easily be made good if necessary later.

With this assumption we have for the upper surface ($r=0$)

$$T_0 = T_0^{(1)} + T_0^{(2)},$$

$$S_0 = S_0^{(1)} + S_0^{(2)},$$

and for the lower surface

$$0 = S_0^{(1)} e^{i\alpha\rho} + S_0^{(2)} e^{-i\alpha\rho}$$

if it is assumed that there is no wave reflected from the $(\rho+1)$th plane. The crystal waves are denoted by superscripts.

Equation (4) enables these equations to be written in the form

$$T_0 = T_0^{(1)} + T_0^{(2)},$$
$$S_0 = \omega_1 T_0^{(1)} + \omega_2 T_0^{(2)},$$
$$O = \omega_1 e^{i\alpha\rho} T_0^{(1)} + \omega_2 e^{-i\alpha\rho} T_0^{(2)}.$$

The elimination of the unobserved crystal waves $T_0^{(1)}$ and $T_0^{(2)}$ from these three equations yields

$$\frac{|S_0|^2}{|T_0|^2} = 2\omega_1^2 . \omega_2^2 . \frac{1-\cos 2\alpha\rho}{\omega_1^2+\omega_2^2-2\omega_1\omega_2 \cos 2\alpha\rho} \quad (5)$$

This is the so-called " pendulum solution " of the Ewald and Bethe theories. This type of solution was not obtained by Darwin because he neglected one of the solutions on the grounds that a small amount of absorption would make it become infinite for an infinitely thick crystal. The above type of " pendulum " solution is, however, perfectly general, and expressions for the reflexion coefficients of both thick and thin crystals may be deduced from it without the necessity of introducing any true absorption at all.

Nevertheless, the introduction of true absorption is certainly justifiable physically, and in the case of electron diffraction it is probably essential that this should be done in order to obtain reasonable agreement with experiment. The Bethe theory in which absorption is left entirely out of account does not take sufficient cognizance of one of the essential differences between the diffraction of electrons and of X-rays.

Before we introduce absorption, however, we shall for the purpose of the later discussion proceed to deduce the formulæ which correspond in this form of the theory to the Bethe case.

### *The Thick Crystal.*

The periodic fluctuations in the intensity of the reflected beam which are indicated by the above expression (5) are not observed in practice for this reason. If $\rho$ is very large, small variations in $\alpha$ due to fluctuations in the velocity of the incident electrons will make the cosine term run through all its possible values from $-1$ to $+1$, so that which is observed is rather the average value of the expression (5) taken over its period.

We hence take as the observed value of $|S_0|^2/|T_0|^2$,

$$\frac{|S_0|^2}{|T_0|^2} = \frac{2\omega_1^2\omega_2^2\alpha}{\pi}\int_0^{\pi/\alpha} \frac{1-\cos 2\alpha\rho}{\omega_1^2+\omega_2^2-2\omega_1\omega_2\cos 2\alpha\rho}d\rho.$$

In this averaging process we may with sufficient accuracy treat $\rho$ as a continuous variable, and the integration gives

$$\frac{|S_0|^2}{|T_0|^2} = \omega_1\omega_2\left\{1-\frac{\omega_1-\omega_2}{\omega_1+\omega_2}\right\} = \left\{1-\sqrt{1-\frac{P^2}{v-P}}\right\}. \quad . \quad . \quad . \quad (6)$$

This expression is valid outside the region of total reflexion given by $0 \leqslant v \leqslant 2P$.

*The Thin Crystal.*

The process of averaging by which the formula for the thick crystal was deduced from the general expression (5) is clearly no longer valid if both $\alpha$ and $\rho$ are small. In this case we may expand the cosine in the denominator and find

$$\frac{|S_0|^2}{|T_0|^2} = 4\omega_1^2\omega_2^2\cdot\frac{\sin^2\alpha\rho}{(\omega_1-\omega_2)^2+4\alpha^2\rho^2} = \frac{\sin^2\alpha\rho}{\alpha^2/P^2+\alpha^2\rho^2}, \quad (7)$$

since $\omega_1\omega_2=1$.

If $\rho^2 << 1/P^2$, and if $v$ is small, we may write

$$\frac{|S_0|^2}{|T_0|^2} = P^2\cdot\frac{\sin^2\alpha\rho}{\sin^2\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which is simply the Laue formula for the reflexion as deduced on the assumption that there is no interaction between the incident and scattered waves. This formula is of little practical interest, however, since in the case of electrons the interaction is really always large, and approximations which may be valid for X-rays break down for this reason in the electron case.

In the derivation of the above formulæ (7) and (8) it is assumed that $v$ is small. For high voltage electrons in which we are primarily interested this is not so, and we must derive a more accurate expression to replace (8) when $v$ is large.

In this case it is convenient to start from the fundamental equation

$$DS_{r+2}+[(R^2-D^2)e^{iv}-e^{-iv}]S_{r+1}+DS_r=0,$$

corresponding to the equation (3) for $T_r$.

This equation reduces to

$$S_{r+2}-2(-)^n[\cos v+P\sin v]S_{r+1}+S_r=0,$$

which is satisfied by the substitution

$$S_r=(-)^{nr}x^rS_0,$$

provided $x$ satisfies the quadratic

$$x^2-2ux+1=0,$$

where

$$u=\cos v+P\sin v.$$

We hence find that

$$x_{1,2}=u\pm i\sqrt{1-u^2}=e^{\pm i\phi},$$

if we put

$$\cos\phi=u, \quad \sin\phi=+\sqrt{1-u^2}.$$

The general solution is then of the form

$$S_r=(-)^{nr}[\alpha e^{ir\phi}+\beta e^{-ir\phi}],$$

where $\alpha$, $\beta$ are constants to be determined from the boundary conditions $S_r=S_0$, when $r=0$, and $S_m=0$, if the thin crystal has $m$ planes.

We obtain

$$S_r=(-)^{nr}\operatorname{cosec} m\phi.\sin(m-r)\phi.S_0,$$

and on substituting back in (1) we find that

$$\frac{S_0}{T_0}=\frac{R}{1-De^{iv}[\cos\phi-\cot m\phi.\sin\phi]},$$

whence

$$\frac{|S_0|^2}{|T_0|^2}=\frac{P^2\sin^2 m\phi}{P^2\sin^2 m\phi+\sin^2\phi}. \quad . \quad . \quad . \quad (9)$$

When $u=1$, the numerator and denominator of this expression vanish ; but

$$\operatorname*{Lim}_{u\to 1}\frac{|S_0|^2}{|T_0|^2}=\frac{P^2m^2}{P^2m^2+1}.$$

5. *The Thick Crystal with Absorption.*—$h \neq 0$, $a_{r+2} = a$ (a constant).

We solve equation (3) as before by setting

$$\left.\begin{aligned} T_r &= T_0 x^r, \\ x &= (-)^n(1-\epsilon), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and find for $\epsilon$

$$\epsilon^2 = -v(v-2P) + h^2 - 2ih(v-P), \quad . \quad . \quad (11)$$

if $v$ is small. If $v$ is not small, we have to use the complete form of the quadratic for $x$ as obtained from equation (3).

In this case one of the two solutions has an amplitude which increases with the thickness of crystal traversed, and the other diminishes with the thickness. As a proper function of the problem, that solution must be chosen for which $|x| < 1$. This is done by taking the root of $\epsilon^2$ for which the real part is positive.

From equation (1) we then find

$$S_r = \frac{(-)^{nr} R x^r T_0}{1-(D-h)x(-)^n e^{iv}},$$

and in particular

$$\frac{S_0}{T_0} = \frac{R}{1-(D-h)x(-)^n e^{iv}} \quad . \quad . \quad . \quad . \quad (12)$$

In practice it is most convenient to calculate values of $x$ from equations (10) and (11) with the aid of tables of complex roots (*e. g.*, Jahnke-Emde, Funktionentafeln), and then find $|S_0/T_0|^2$ from the numerical value of $S_0/T_0$ so obtained.

6. *The General Solution.*—Some of the formulæ of sections (4) and (5) are naturally very similar to those obtained by Darwin (*loc. cit.*) for the X-ray case, except where the difference between his formulæ and ours has been specially noted. In this section we proceed to develop formulæ for a more general case which was not treated by Darwin, and which is of special interest in electron diffraction problems.

From the fundamental equations (1) and (2) we find by elimination

$$(D-h)e^{ik(a_{r+3}-a_{r+2})\sin\theta} S_{r+2} + [\{R^2-(D-h)^2\}e^{ika_{r+2}\sin\theta} - e^{-ika_{r+2}\sin\theta}]S_{r+1} + (D-h)S_r = 0$$

and

$$(\mathrm{D}-h)e^{-ik(a_{r+3}-a_{r+2})\sin\theta}\mathrm{T}_{r+2}$$
$$+[\{\mathrm{R}^2-(\mathrm{D}-h)^2\}e^{ika_{r+2}\sin\theta}-e^{-ika_{r+2}\sin\theta}]\mathrm{T}_{r+1}+(\mathrm{D}-h)\mathrm{T}_r=0.$$

We write the latter equation in the form

$$\mathrm{T}_{r+2}+p(r)\mathrm{T}_{r+1}+q(r)\mathrm{T}_r=0, \quad . \quad . \quad . \quad (13)$$

where

$$p(r)=(\mathrm{D}-h)^{-1}[\mathrm{R}^2-(\mathrm{D}-h)^2-e^{-2ika_{r+2}\sin\theta}]e^{ika_{r+3}\sin\theta},$$
$$q(r)=e^{ik(a_{r+3}-a_{r+2})\sin\theta}.$$

For the particular applications which we have in view $p(r)$ and $q(r)$ tend to constant limiting values for large $r$, if $r$ is measured from the crystal surface, and in actual practice we shall assume that $p(r)$ and $q(r)$ will reach their limiting values fairly rapidly as $r$ increases.

If we make these assumptions the difference equation is of the Poincaré type, and a solution which is convenient for our purpose may be obtained in the form of a continued fraction.

The equation (13) may be written in either of the two forms

$$\frac{\mathrm{T}_{r+1}}{\mathrm{T}_r}=-\cfrac{q(r)}{p(r)+\cfrac{\mathrm{T}_{r+2}}{\mathrm{T}_{r+1}}}, \quad . \quad . \quad . \quad . \quad (14)$$

or

$$\frac{\mathrm{T}_r}{\mathrm{T}_{r+1}}=-\cfrac{1}{p(r-1)+q(r-1)\cfrac{\mathrm{T}_{r-1}}{\mathrm{T}_r}}. \quad . \quad . \quad (15)$$

The repeated application of the above formulæ leads to the expression of $\mathrm{T}_{r+1}/\mathrm{T}_r$ in terms of one or other of the continued fractions

$$\frac{\mathrm{T}_{r+1}}{\mathrm{T}_r}=-\cfrac{q(r)}{p(r)-\cfrac{q(r+1)}{p(r+1)-\cfrac{q(r+2)}{p(r+2)-\ldots}}} \quad . \quad . \quad (14')$$

or

$$\frac{\mathrm{T}_r}{\mathrm{T}_{r+1}}=-\cfrac{1}{p(r-1)-\cfrac{q(r-1)}{p(r-2)-\cfrac{q(r-2)}{p(r-3)-\ldots}}} \quad . \quad (15')$$

In the limit when $r \to \infty$, the coefficients of the difference equation become constants $p(\infty)$ and $q(\infty)$. The equation with constant coefficients has as its characteristic equation

$$t^2 + p(\infty)t + q(\infty) = 0$$

with roots $a_1$, $a_2$.

If

$$|a_1| < |a_2|$$

it may be shown that

$$\underset{r \to \infty}{\text{Lim.}} \frac{T_{r+1}}{T_r} = a_1,$$

where $T_{r+1}/T_r$ is given by the former equation (14′). The second expression (15′) reduces to the larger root in the limit.

We shall assume that when a small perturbation is introduced, such as a distortion of the upper plane spacing, the physically admissible value for $T_{r+1}/T_r$ is given by equation (14′). The actual function $T_r$ may be obtained from the first order equation by a single summation.

The right-hand side of equation (14′) is a known function of $r$, $\phi(r)$ say. Taking logarithms of both sides gives

$$\Delta \log T_r = \log \phi(r),$$

where $\Delta$ is the usual difference operator, and a summation yields the solution

$$T_r = \exp \overset{r}{\underset{a}{S}} \log \phi(z) \Delta z,$$

where the operator $\overset{r}{\underset{a}{S}}$ is defined by Nörlund [9] as follows :

$$\overset{r}{\underset{a}{S}} \phi(z)\Delta z = \underset{\mu \to 0}{\text{Lim.}} \left\{ \int_a^\infty \phi(t) e^{-\mu\lambda(t)}\, dt - \sum_{s=0}^{\infty} \phi(x+s) e^{-\mu\lambda(x+s)} \right\},$$

provided that for variable $x$, values of $p \geqslant 1$ and $q \geqslant 0$ may be found such that for $\log \lambda(x) = x^p . (\log x)^q$,

$$\int_c^\infty \phi(t) e^{-\mu\lambda(t)}\, dt, \qquad \sum_{s=0}^{\infty} \phi(x+s) e^{-\mu\lambda(x+s)},$$

both converge for $\mu > 0$.

For many purposes it will be found, however, that the explicit expression for $T_r$ is not required, and it will be sufficient to know the ratio $T_1/T_0$ as we shall now show.

From the second fundamental equation (2) we have

$$S_{r+1}e^{ika_{r+2}\sin\theta} = R^{-1}e^{-ika_{r+2}\sin\theta}T_{r+1} - R^{-1}(D-h)T_r,$$

and if this is substituted in (1) there results

$$S_r = [R - R^{-1}(D-h)^2]T_r + R^{-1}(D-h)e^{-ika_{r+2}\sin\theta}T_{r+1},$$

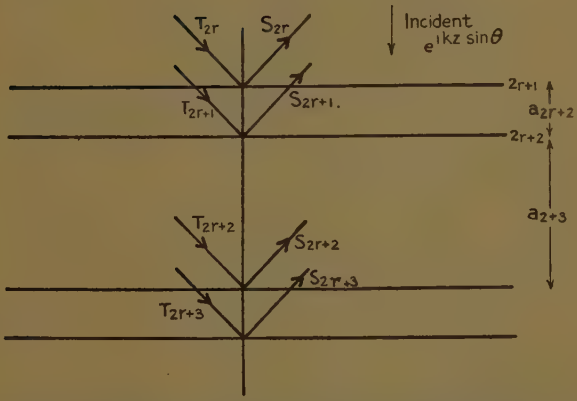
and in particular

$$\frac{S_0}{T_0} = [R - R^{-1}(D-h)^2] + R^{-1}(D-h)e^{-ika_2\sin\theta}\frac{T_1}{T_0},$$

where $T_1/T_0$ is obtained from (14′)

$$\frac{T_1}{T_0} = -\cfrac{q(0)}{p(0) - \cfrac{q(1)}{p(1) - \cfrac{q(2)}{p(2) - \ldots}}} \quad . \quad . \quad . \quad (16)$$

Fig 4.




In practice this series may be terminated after a few terms by substituting the asymptotic value of $T_{r+2}/T_{r+1}$ for $-q(r)/p(r)$—.

7. *Application to a Crystal Structure with a Base.*—The foregoing method may clearly be applied if the crystal has a base structure within the fundamental cell. For definiteness we may consider the case of diamond when we are investigating the reflexions from atomic planes parallel to the (111) natural face. The fundamental spacing is then divided in the ratio of three to one by the base plane and the whole crystal acts as two interlocking

sets of simply spaced planes. If the spacing of the upper planes of the crystal differs from that of the body of the crystal, it is convenient to divide the equations into two sets, and in the general case into as many sets as there are base planes.

The fundamental equations become

$$S_{2r+1} = RT_{2r+1} + (D-h)e^{ika_{2r+3}\sin\theta}S_{2r+2}, \quad (17)$$

$$T_{2r+1}e^{-ika_{2r+2}\sin\theta} = (D-h)T_{2r} + RS_{2r+1}e^{ika_{2r+2}\sin\theta}, \quad . \quad (18)$$

$$S_{2r+2} = RT_{2r+2} + (D-h)e^{ika_{2r+4}\sin\theta}S_{2r+3}, \quad (19)$$

$$T_{2r+2}e^{-ika_{2r+3}\sin\theta} = (D-h)T_{2r+1} + Re^{ika_{2r+3}\sin\theta}S_{2r+2}. \quad (20)$$

By elimination we find

$$T_{2r+4} + p(r)T_{2r+2} + q(r)T_{2r} = 0, \quad . \quad . \quad . \quad (21)$$

where

$$\begin{aligned} p = -e^{ik(a_{2r+4}+a_{2r+5})\sin\theta}[&(D-h)^{-2}\{R^2-(D-h)^2 \\ &-e^{-2ika_{2r+4}\sin\theta}\}\{R^2-(D-h)^2-e^{-2ika_{2r+3}\sin\theta}\} \\ &-e^{-2ika_{2r+4}\sin\theta}-e^{-2ika_{2r+3}\sin\theta}\{R^2-(D-h)^2 \\ &-e^{-2ika_{2r+4}\sin\theta}\}\{R^2-(D-h)^2-e^{-2ika_{2r+2}\sin\theta}\}^{-1}], \end{aligned}$$

$$\begin{aligned} q = e^{ik(a_{2r+4}+a_{2r+5}-a_{2r+2}-a_{2r+3})\sin\theta}&\{R^2-(D-h)^2 \\ &-e^{-2ika_{2r+4}\sin\theta}\}\{R^2-(D-h)^2-e^{-2ika_{2r+2}\sin\theta}\}^{-1}. \end{aligned}$$

Equation (21) may be written in the form

$$\frac{T_{2r+2}}{T_{2r}} = -\cfrac{q(r)}{p(r)+\cfrac{T_{2r+4}}{T_{2r+2}}}. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

We finally find

$$\begin{aligned} \frac{S_0}{T_0} = R - R^{-1}(D-h)^2\Big[1 + e^{-ika_2\sin\theta}&\{R^2-(D-h)^2 \\ &-e^{-2ika_2\sin\theta}\}^{-1}\left\{e^{-ika_2\sin\theta}+e^{-ika_3\sin\theta}\frac{T_2}{T_0}\right\}\Big], \end{aligned} \quad (23)$$

where $T_2/T_0$ is given by the continued fraction

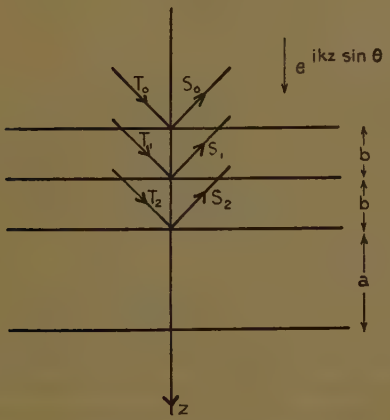
$$\frac{T_2}{T_0} = -\cfrac{q(0)}{p(0)-\cfrac{q(1)}{p(1)-\cfrac{q(2)}{p(2)-\ldots}}}, \quad . \quad . \quad (24)$$

which again may be terminated after the first few terms by using the asymptotic value of $T_{2r+4}/T_{2r+2}$.

If the distorted planes are not formed out of the crystal itself; but are due to layers of gas or other material on the surface of the crystal, the appropriate alterations must be made in the values of R, D, and $h$ in the equations, while for the asymptotic value of $T_{2r+4}/T_{2r+2}$ the value appropriate to the crystal must be used.

8. *The Simple Case of Two Contracted Planes of Equal Spacing.*—The values of the parameters occurring in the theory are at present so little known that for the

Fig. 5.




purpose of an estimate of the magnitude of the effects it is sufficiently accurate to base the calculations on a simplified model in which the contracted planes all have an equal spacing and are few in number. The case of just two contracted planes is of particular interest in the discussion in the next section of the experimental results, and the appropriate formulæ may be obtained very simply by fitting together at the interface the solutions proper to the two parts.

The equations are

$$S_0 = R'T_0 + (D'-h')S_1 e^{ikb \sin\theta}, \quad . \quad . \quad . \quad (25)$$

$$T_1 e^{-ikb \sin\theta} = (D'-h')T_0 + R'S_1 e^{ikb \sin\theta}, \quad . \quad . \quad (26)$$

$$S_1 = R'T_1 + (D' - h')S_2 e^{ikb \sin\theta}, \quad . \quad . \quad . \quad (27)$$

$$T_2 e^{-ikb \sin\theta} = (D' - h')T_1 + R'S_2 e^{ikb \sin\theta}, \quad . \quad . \quad (28)$$

$$S_2 = \omega T_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The value of $\omega$ in equation (29) is taken from the previous treatment of the semi-infinite crystal (eqn. 12, section 5). In these equations the values of R, D, and $h$ for the upper planes are denoted by a dash ($'$).

From these equations it is found that

$$\frac{S_0}{T_0} = \alpha^{-1}(D' - h')^2 + R', \quad . \quad . \quad . \quad . \quad (30)$$

where

$$\alpha = \left[ \frac{e^{-2ikb \sin\theta} - \omega R'}{R' - \omega\{R'^2 - (D' - h')^2\} e^{2ikb \sin\theta}} - R' \right].$$

## Part II.

### *The Breadth of the Region of Selective Reflexion.*

Reference may be made to the original paper (*loc. cit.*) for fuller details ; but the broad features of the reflexions in diamond as observed by Beeching are as follows. The peaks corresponding to the various orders are strongly asymmetrical and are very steep on the short wave-length side. For 40 K.V. electrons the half-intensity breadth in the third order (333) reflexions from a (111) natural face of diamond is about 30′. After the maximum the intensity decreases till the reflected spot disappears (or almost disappears) at about two-thirds the distance from one order to the next, when it again sets in rather sharply. The second order spectrum, which is forbidden by the structure factor, appears relatively more strongly than in the X-ray case.

The breadth of the reflexion region in the case quoted above should be about 2′ according to the Bethe theory, so there is a considerable discrepancy to be accounted for. This discrepancy cannot be accounted for by the comparatively crude method we (and others) have employed to calculate the Fourier coefficients of the crystal potential. It is clear that if the tetrahedral structure of the carbon atom is taken into account, and if a certain amount of overlapping between adjacent atoms in the diamond crystal is allowed for, the ordinary structure factor may be considerably modified, and orders such as the second

order in the case of diamond may be allowed by the more accurate form [10]; but the change in the Fourier coefficients would not be sufficient to affect the present discussion. Nor can the effect be attributed to the absorption of the incident beam in the crystal with the consequent lack of deep penetration, because it is known that absorption actually diminishes the breadth of the selective region, although it does produce the right type of asymmetry.

The general features of the intensity curves strongly suggest that the pattern is in the main produced by the action of a very few planes of the crystal. Since theory indicates a penetration which is several times this amount, and which would make the breadth very small, the most natural assumption to make about the process is that a few planes at the surface of the crystal are partly out of phase with respect to the rest of the crystal. Now this effect may be obtained in two ways. In the first place the theory of crystal cohesion tells us that there must be a contraction of the crystal spacing near the surface. In polar crystals numerical estimates of this contraction have been made by Lennard-Jones [11] and others; but for a diamond-like lattice the calculations are much more troublesome and have not yet been carried out. Nevertheless, we may by analogy expect a contraction of the surface spacing by a few per cent., but owing to the short range of the exchange forces it seems probable that we cannot, *a priori*, expect an appreciable contraction over more than the first one or two planes.

The second possibility is that there is a layer of foreign material on the surface of the crystal which remains adsorbed to the surface in a stable form even under the relatively low pressures employed in this work and in spite of the bombardment of the surface by the electron beam.

The first effect must be present although we cannot be sure of its magnitude; and in view of the difficulty which is experienced by workers in various fields in getting their surfaces free of gas, it would be rather surprising if no gas were present on crystal surfaces under the conditions in which electron diffraction experiments are carried out, unless, as has often been assumed, the electron beam itself is a very efficient "degasser" of the surface.

On the basis of the present theory calculations were

first made to estimate the effect on the intensity of the reflected beam which would be produced by contracting the spacing of one or two planes at the crystal surface. Unfortunately, the number of parameters involved is rather large and their probable values only approximately known; but the results indicated that the equilibrium distortion at the surface of the diamond crystal is insufficient to explain the results unless the distortion is larger and extends over more planes than one would expect from Lennard-Jones's work on polar crystals.

It seems probable that the required phase jump between the upper planes and the lower planes will be greater if the upper planes are composed of atoms of a different kind from those of the diamond crystal itself, since we may suppose that the surface of discontinuity is more pronounced in this case, and that a good deal of diffuse scattering may take place in this plane. The most effective scattering gas which is likely to be present on the crystal surface is oxygen, and it seems reasonable to assume the existence of a monomolecular layer of the gas to see if this is capable of explaining the experimental results.

In our model we have represented this rather crudely by assuming the existence of two layers of gas on the crystal surface and by assuming that the spacing is 10 per cent. smaller than that of the diamond crystal. The reflexion coefficient per layer of the gas has been taken as one and a half times that for a plane of carbon atoms to allow for the increased reflexion coefficient of oxygen. There is also likely to be an increase in reflexion from the plane of separation between the two parts. The absorption in the oxygen layers has also been taken as one and a half times that in a plane of carbon atoms.

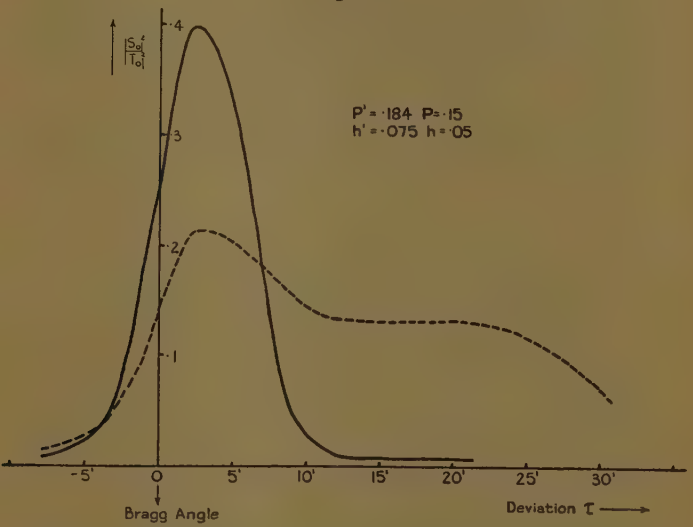
The present theory gives a half-breadth equal to $P/ka \cos\theta_B$ in the case of the simple undistorted lattice with no absorption, and if this is compared with the breadth predicted by the Bethe theory we find that P must be taken as ·072 for the (333) reflexion to obtain the same half-breadth from the two theories. The value which should be taken for the absorption coefficient $2h$ is rather difficult to estimate, and the value of $h$ which we have assumed is an approximate figure based on the mean free path for ionization in a solid, and also on experimental data obtained by passing electrons through thin films [12].

Owing to the uncertain values of the parameters we have not thought it worth while to carry through the calculations with the more elaborate formulæ of the preceding part of the paper, and have consequently used the simple expression (30).

The general features of the calculation are illustrated by the curves in fig. 6.

The full curve is based on a value for P of ·15, so that the reflexion coefficient we have taken is about four times the theoretical value. The dotted curve then represents

Fig. 6.




the intensity distribution when the gas layers are present, while the full curve represents the intensity distribution when the gas layers are removed and there is no cohesive contraction of the surface spacing. The dotted curve shows the type of asymmetry which is experimentally observed, and the spread is of the right order of magnitude to explain the observed results.

Obviously too much attention need not be paid to the actual numerical values of the reflexion coefficient $|S_0/T_0|^2$; but the results indicate that in the diffraction of fast electrons the spacing and nature of the surface planes are most important.

*Summary and Conclusion.*

A theory of electron diffraction based on that of Darwin for the case of X-rays has been developed, and Darwin's equations have been generalized to allow for an arbitrary arrangement of planes near the crystal surface. On the basis of this theory an attempt has been made to explain the observed discrepancy in the experimental breadth of the region of selective reflexion and that predicted by the Bethe theory. It is shown that the general features of the experimental results may be obtained by assuming that a few planes near the surface have a contracted spacing relative to that of the crystal interior. The magnitude of the effect suggests that these contracted planes are due to a gas layer on the surface rather than to a contraction of the crystal itself near the surface.

I wish to express my thanks to Professor G. P. Thomson for suggesting this problem and for many valuable discussions during the course of the work.

*References.*

(1) *Ann. d. Physik*, lxxxvii. p. 55 (1928).
(2) Phil. Mag. xxvii. pp. 315, 675 (1924) ; xliii. p. 800 (1922).
(3) *Ann. d. Physik*, xlix. pp. 1, 117 (1916) ; liv. pp. 519, 557 (1917),
(4) R. Beeching, Phil. Mag. xx. p. 841 (1935).
(5) Sc. Papers, Tokio Inst. Phys. Chem. Res. xxvi. p. 225 (1935).
(6) *Handbuch der Physik*, xxiv, 2, p. 628 *et seq.*
(7) Phys. Rev. xxxv. p. 1310 (1930).
(8) Proc. Roy. Soc. A, cxxx. p. 499 (1931).
(9) Nörlund, 'Differenzenrechnung,' p. 43.
(10) A paper on this subject by Ewald and Hönl is to appear in the *Ann. d. Physik*.
(11) Proc. Roy. Soc. A, cxxx. p. 499 (1930).
(12) G. P. Thomson, Phil. Mag. xviii. p. 649 (1934).

South Kensington.
October 1936.

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## XXIX. *Adsorption Forces and their Electrical Nature.*—III.* *On the Nature of the Forces of Wetting.* *By* B. W. Iliin, A. A. Leontiew, *and* S. W. Bragin †.

THE determination of the heat of wetting of powders which have *a geometrical external* (*non porous*) *surface* becomes of great interest when we investigate

* B. W. Iliin, Phil. Mag. xlviii. p. 193 (1924) ; l. p. 1144 (1925).
† Communicated by the Authors.

the process which takes place at the boundary of the solid and liquid phases. Such determination is also of great importance in the case of *a theoretical computation of the work (energy) of wetting.*

### I. *The Method of Preparation of Powders.*

As a sample of such powders we have tried to use alkali salts of halogen acids (mainly the salts of potassium, KCl, KBr, KI) and also barium sulphate ($BaSO_4$) of different mesh. For obtaining alkali salts of halogen acids (KCl, KBr, KI) we let them precipitate from solutions or grounded ready made preparations. The results obtained by this method were not satisfactory, due to the fact that the salts in the precipitates readily stick together, the separate grains grow into larger aggregates of irregular form, and the drying and sieving of them become very difficult. When examined under a microscope the surface of such powders proved to have many defects—cracks and fissures. Except this the sample of powder always contained some fine crystalline dust. We had no possibility of applying the method of sublimation * or the method of Brentano †. Therefore the heat of wetting of the alkali salts of halogen acids could be determined only approximately. When preparing the barium sulphate powders ($BaSO_4$) we aimed to have no defects of the surface and to make them of uniform structure, *i. e.*, consisting of grains nearly of the same size and containing no fine crystalline dust. The most reliable method for obtaining such powders proved to be *the method of von Weimarn* ‡. Applying this method we obtained barium sulphate ($BaSO_4$) by means of mixing together the reacting solutions of barium sulphocyanate and manganese or cobalt sulphate.

The following reaction of a double interchange takes place :—

$$Ba(CNS)_2 + MnSO_4 = \underset{\text{precipitate}}{BaSO_4} + Mn(CNS)_2$$

or

$$Ba(CNS)_2 + CoSO_4 = \underset{\text{precipitate}}{BaSO_4} + Co(CNS)_2.$$

* Johnson and Maas, Journ. Am. Chem. Soc. xlix. (1927).

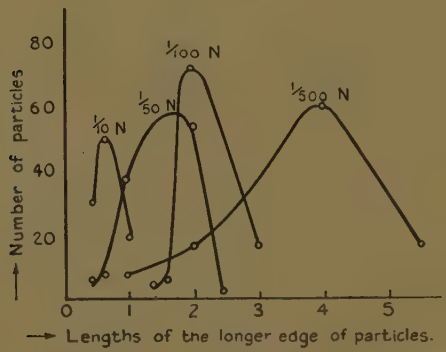
† Brentano, Phil. Mag. iv. p. 620 (1927).

‡ Von Weimarn, Journ. Russ. Phys.-Chem. Soc. xl. (40), 1908 (Russian).

If the conditions in all the cases are identical the fineness of the precipitate will depend on the concentration of the solution from which they precipitate. We took the following concentrations :—0·2 N ; 0·18 N ; 0·15 N ; 0·12 N ; 0·1 N ; 0·02 N ; 0·01 N ; 0·002 N. The fineness of the powder will decrease when the concentration of the reacting solutions decreases.

All the chemicals used were previously analysed in order to avoid the presence of any impurities, and were rectified if necessary. The $BaSO_4$ powders produced by this method were repeatedly washed in water and dried to a constant weight at 130°–150° C.

Fig. 1.




The $BaSO_4$ powders (in water) when examined under a microscope were found to consist of particles nearly all of them of the same size and having a prismatic form, in most of the cases with a square as the base. The curve of distribution (fig. 1), where the lengths of the longer edge of the prism is plotted as abscissa and the number of prisms with the given edge as the ordinate, shows that the structure of our powders is sufficiently uniform. Knowing the average size of separate crystals it is not difficult to calculate their surface, and, using the curve of distribution, to determine the surface of one gram of powder of barium sulphate ($BaSO_4$) of given mesh, *i. e.*, its specific surface. In our experiments the specific surface varied from 2000 cs.²/gram to 16,000 cm.²/gram.

## II. *Measuring of the Heat of Wetting.*

The heat of wetting of the crystalline powders was measured with the aid of a microcalorimeter and a resistance thermometer, which was wound around a silver calorimetric vessel because the quantity of powder under investigation was small. The thermometer was connected to a Wheatstone bridge supplied with a mirror reading galvanometer $\left(\text{Siemens and Halske } 5 \cdot 10^{-9} \frac{\text{Å}}{\text{mm}}\right)$. The cord of the bridge was made of a thick manganin wire, and manganin coils (each 200 ohm) were attached to each end. The ballast resistance made it possible to obtain a marked displacement of the sliding contact even when the change of the potential applied to the cord was small. The displacement of the contact was calibrated in calories according to the amount of Joule heat evolved in the calorimeter by a special heater (manganin wire with a resistance of 1·875 ohm). In all the experiments a correction for radiation had to be made.

This arrangement was very sensitive even to very small thermal effects.

The following data were obtained from measuring of the heat of wetting of KCl, KBr, and KI by tetrachloric carbon ($CCl_4$).

TABLE I.

| Salts. | KCl. | KBr. | KI. | The powders were sieved. |
|---|---|---|---|---|
| The heat of wetting by $CCl_4$ in small calories per gram. | 0·055 | 0·046 | 0·039 | through a sieve 900 mesh per cm.². |
| | 0·063 | 0·052 | 0·46 | through a sieve 3600 mesh per cm.². |

The different values of heat of wetting of $BaSO_4$ were determined by using three liquids—water, ethyl alcohol, and tetrachloric carbon ($CCl_4$). All the liquids had been rectified by distillation, and ethyl alcohol and $CCl_4$ had been dried as well. The results of the experiments taken as an average of several sets of measurements (10–15 separate measurements in each set) are given in the summary (Table II.) and plotted on the diagram (fig. 2). The heat of wetting is calculated in small calories per gram of absorbent. The values of the specific surface,

determined according to the method described above, are given in the last column of Table II. measured in square

Fig. 2.

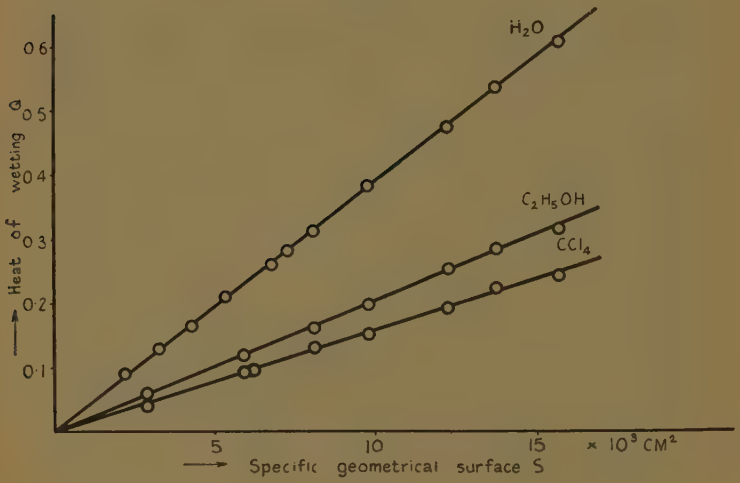



TABLE II.

| The concentration of solution. | Heat of wetting in small calories per gram. | | | The specific surface in cm.²/gram. |
|---|---|---|---|---|
| | $H_2O$. | $C_2H_5OH$. | $CCl_4$. | |
| 1/500 N ..... | 0·09 | — | — | 2200 |
| 1/500 „ ..... | — | 0·06 | 0·04 | 2900 |
| 1/100 „ ..... | 0·13 | — | — | 3300 |
| 1/50 „ ..... | 0·17 | — | — | 4300 |
| 1/100 „ ..... | 0·21 | — | — | 5400 |
| 1/20 „ ..... | — | 0·12 | 0·09 | 5900 |
| 1/50 „ ..... | — | — | 0·09 | 6100 |
| 3/20 „ ..... | 0·26 | — | — | 6800 |
| 1/10 „ ..... | 0·28 | — | — | 7300 |
| 1/10 „ ..... | 0·32 | 0·16 | 0·13 | 8100 |
| 3/25 „ ..... | 0·38 | 0·20 | 0·15 | 9800 |
| 3/20 „ ..... | 0·47 | 0·25 | 0·19 | 12300 |
| 18/100 „ ..... | 0·53 | 0·28 | 0·22 | 13800 |
| 1/5 „ ..... | 0·60 | 0·31 | 0·24 | 15700 |

centimetres per 1 gram of adsorbent. This table shows also the concentrations of " solutions " for each precipitate respectively.

During a second series of experiments, made two months later, when not all the conditions of the precipitation were identical, it was found that, in spite of the fact that a solution of the same concentration was used, the mesh, the specific surface, and the values of the heat of wetting were quite different.

Plotting on the diagram the data of the values of *the heat of wetting against their specific geometrical surface we get for all the three tested liquids a direct proportionality between them.* This relation is shown by the straight lines which pass through the beginning of the coordinates (see fig. 2). The slope of the straight lines gives the value of the heat of wetting in small calories per square centimetre of surface of adsorbent. For water this value equals $3{\cdot}8.10^{-5}$ $\frac{\text{small calories}}{\text{cm.}^2}$, for ethyl alcohol $2.10^{-5}$ $\frac{\text{small calories}}{\text{cm.}^2}$, and for $CCl_4$ $1{\cdot}5.10^{-5}$ $\frac{\text{small calories}}{\text{cm.}^2}$; hence for water it is 2·6 times as much as for $CCl_4$ and nearly twice as much as for ethyl alcohol.

### III. *Discussion of the Results and Theoretical Computation of the Work of Wetting.*

Table I. shows that the difference of the values of the heat of wetting for powders of halogen salts of potassium KCl, KBr, and KI reached only 18 per cent. when sieved through sieves of 900 and 3600 mesh per square centimetre. Such a small difference can be explained mainly by the presence of small fragments of crystals.

The fact that our $BaSO_4$ powders were not porous is shown by the strict proportionality between the heat of wetting of $BaSO_4$ and the geometrical surface of the adsorbent when the surface is calculated from the sizes of separate grains and by the use of the curves of distribution of the grains by their length.

Generally the presence of pores in small crystals of barium sulphate is hardly probable.

The measured values of the specific surface of the $BaSO_4$ powders were found to be very small (fractions of a square metre), and for the finest powder reached 1·6 square metre per gram. In measuring the adsorption of alizarin by $CaF_2$ powders de Boer * found the values

* De Boer, *Zeits. phys. Chem.* xiii. p. 15 (1931).

of the specific surface to be small, of the order of fractions of a square metre (0·8 m.$^2$ per gram) *.

In order to check the experimental data of the heat of wetting Miss A. A. Leontiew made a theoretical computation of the work of wetting. The total energy of the interaction between the ions of the crystalline lattice and dipole liquid (water) consist first of all of a purely electrostatic effect of interaction between the rigid dipole and the lattice, second of the dispersion effect (according to Polanyi and London †), and third of the induction effect ‡. In case we have polar liquids and a crystalline adsorbent with an ionic lattice the *electrostatic dipole effect will prevail over both the dispersion and induction effects.* According to an approximate calculation § the dispersion effect of London for a $BaSO_4$-water system with the surface of 16,000 cm.$^2$ per gram equals roughly $0{\cdot}03 \frac{\text{small calories}}{\text{gr. of powder}}$. Therefore when making a first rough calculation of the work of wetting we can confine ourselves only to the electrostatic dipole effect.

Assuming this, we find the work of the removal of the first adsorption layer from the surface of the adsorbent may be computed by the following formula:

$$W = \int_{r_0}^{\infty} \frac{N.2\mu.\Sigma e.dr}{r^3} = \frac{N.\mu.\Sigma e}{r_0^2}, \quad . \quad . \quad (1)$$

where $\mu$ is the moment of the dipole, $r_0$ the distance between the centre of the ion and the centre of the dipole, N is the number of ions on the surface of the powder.

The number N was determined by the following method. In a series of experiments on the adsorption of vapour and liquids by $BaCl_2$ and $CaF_2$, de Boer and his collaborators ||

* The formula for the computation of the surface on the basis of the heat of wetting and the adhesion constant given by Bartell u. Fu in 1920 could not have been used during our experiments, due to the fact that the value of the adhesion constant for barium sulphate and liquids used by us was unknown. *Colloid. Ann.* vii. (1920).

† M. Polanyi u. F. London, *Naturw.* xviii. p. 1099 (1930) ; F. London, *Zeits. phys. Chem.* (B) xi. p. 246 (1931).

‡ See F. Lenel, *Zeits. phys. Chem.* (B) xxiii. p. 379 (1933), and J. de Boer u. J. Custers, *Zeits. phys. Chem.* (B) xxv. p. 225 (1934).

§ The mistake in the computation made both by London and Lenel has been taken into account. See de Boer u. J. Custers, *loc. cit.*, and B. W. Iliin, *Sorena*, 1936, no. 1 (Russian).

|| *Zeits. Phys. Chem.* (B) xiii., xiv., xv. (1932) ; xxiv., xxv. (1934).

have shown that not more than one molecule of the absorptive (for example water) settles on the area occupied by one separate ion of the lattice. According to this one molecule of water settles in one ion of $Ba^{2+}$ or in one complex ion $(SO_4)^{2-}$. Knowing the distance in the $BaSO_4$ lattice between $Ba^{2+}$ and the centre of the tetrahedron $(SO_4)^{2-}$, we see that the area per each ion will equal $12{\cdot}53(Å)^2$. The number of $Ba^{2+}$ ions equal those of $(SO_4)^{2-}$. Consequently, dividing the surface of the powder which has been determined experimentally (by measuring the dimensions of the particles by means of a micrometer in a microscope) by $12{\cdot}53\ (Å)^2$, we get for each powder the required number N.

The distance $r_0$ is defined as the sum of the corresponding ionic radius* and a half of the length of a dipole molecule of water.

The last value can be taken as equal to 1·5 A°. For the $Ba^{2+}$ ion $r_0 = 1{\cdot}43 + 1{\cdot}5 = 2{\cdot}85$ Å. For the $(SO_4)^{2-}$ ion $r_0$ depends upon the position of the adsorbing surface of the tetrahedron of 4 atoms of oxygen between which one atom of sulphur is clamped. The minimal $r_0$ for $(SO_4)^{2-}$ is equal to 3·35 Å, the maximal 4·44 Å.

With the aid of the formula (1) written above two separate calculations of the work of wetting were made, one for the $Ba^{2+}$ ions and another for $(SO_4)^{2-}$, and their sum was taken.

For 1 gram of the $BaSO_4$ powder with a surface of 15,700 cm.$^2$ the computation gave the value of $W_1 = 0{\cdot}54$ small calories per gram, and for 1 gram of $BaSO_4$ with a surface of 2200 cm.$^2$ the value of $W_2 = 0{\cdot}08$ $\frac{\text{small calories}}{\text{gr.}}$

*i. e.*, values of the same order as the ones obtained experimentally for the heat of wetting ($Q_1 = 0{\cdot}60$ $\frac{\text{small calories}}{\text{gr.}}$ and $Q_2 = 0{\cdot}09$ $\frac{\text{small calories}}{\text{gr.}}$ (see Table II.).

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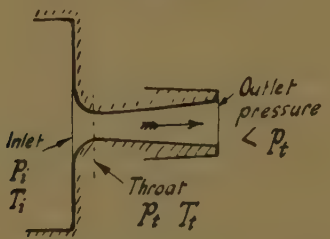
* Van Arkel u. de Boer, *Chemische Bindung* etc., S. 36.

XXX. *The Effect of Variable Specific Heats on the Conditions at the Throat of a Convergent-Divergent Nozzle.* *By* GEORGE G. MCDONALD, *B.Sc., A.M.I.N.A., Lecturer on Engineering, University of Glasgow* *.

*Introduction.*

THE effect of variation with temperature of the specific heats of a gas on the pressure at the throat or narrowest cross-section of a convergent-divergent nozzle (fig. 1) in which the gas is expanding has been

Fig. 1.




investigated by Dr. W. J. Walker in a communication to this Journal †.

Dr. Walker considers the ideal case of the adiabatic expansive flow of a gas from known initial conditions of absolute pressure and temperature to a final pressure lower than the " critical pressure " (which in the case of adiabatic flow takes place at the throat), and establishes an approximation for the " critical pressure ratio," *i. e.*, the ratio of the (unknown) throat absolute pressure to the (known) initial absolute pressure in terms of the (known) specific heats of the gas and the (unknown) throat absolute temperature.

The expression derived, however, while indicating the magnitude of the effect of temperature and variable specific heats on the critical pressure ratio does not allow either the absolute pressure or the absolute temperature at the throat to be calculated directly. If one of these unknowns be eliminated by substituting its value in terms of the

* Communicated by the Author.

† Phil. Mag. ser. 6, xlviii. pp. 703–707 (1924).

other from Poisson's equation, a tedious trial and error calculation still remains before the actual conditions of absolute temperature and pressure at the throat can be determined.

*Synopsis.*

The purpose of the present note is twofold—first, to show how Dr. Walker's approximation may be modified to allow the throat pressure to be calculated directly by the introduction of a close approximation for the throat temperature, and second, to describe a simple and exact graphical method of obtaining the throat temperature from which the throat pressure may be calculated in the ordinary way from Poisson's well-known equation. The two solutions described—the approximate algebraic method and the exact graphical one—are thought to be of technical as well as scientific interest, in view of their practical use in the design of nozzles for certain types of turbine operated by high temperature gases.

---

The specific heats $c_v$ and $c_p$ (C.H.U. per lb.°C.) of the gas, and their ratio $\gamma$ at absolute temperature T (°C.), may be expressed by

$$c_v = a + bT + cT^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$c_p = \left(a + \frac{R}{J}\right) + bT + cT^2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\gamma = \frac{c_p}{c_v} = 1 + \frac{R}{J(a + bT + cT^2)}, \quad . \quad . \quad . \quad . \quad (3)$$

where $a$, $b$, and $c$ are experimental constants, R and J denoting the gas constant (ft. lb. per lb. °C.) and Joule's equivalent (1400 ft. lb. per C.H.U.) respectively.

The velocity of sound, A (ft. per second), in the gas at temperature T is

$$A = (gRT\gamma)^{\frac{1}{2}} = \left\{ gRT\left(1 + \frac{R}{J(a + bT + cT^2)}\right)\right\}^{\frac{1}{2}}. \quad (4)$$

Poisson's law connecting absolute temperature T (°C.) and absolute pressure $p$ (lb./ft.$^2$) during the adiabatic expansion of a gas whose characteristics are given by equations (1) to (3) may be written

$$\frac{T^{\gamma_0} e^{\alpha T + \beta T^2}}{p^{\gamma_0 - 1}} = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\gamma_0=\left(1+\frac{R}{Ja}\right);\quad e=2{\cdot}7183\ ;\quad \alpha=\frac{b}{a}\ ;\quad \beta=\frac{c}{2a}.$$

Let the absolute pressure and temperature at inlet and throat be indicated by $p_i$, $T_i$, and $p_t$, $T_t$, respectively.

Dr. Walker's formula for the critical pressure when expressed in these symbols is

$$p_t=p_i\left(\frac{2}{\gamma_0+1}\right)^{\frac{\gamma_0}{\gamma_0-1}}\left\{1+\frac{3\alpha T_t.(\gamma_0-1)}{4(\gamma_0+1)}\right\},\quad .\quad .\quad (6)$$

$c$ being taken as zero.

This equation can be solved for $p_t$ only when $T_t$ the absolute temperature at the throat is known. A good approximation to the latter is the temperature $T_{t_0}$ at the throat when variation of specific heat with temperature is neglected, *i. e.*,

$$T_t\doteqdot T_{t_0}=T_i\left(\frac{2}{\gamma_0+1}\right)\quad .\quad .\quad .\quad .\quad (7)$$

to a close approximation (since $T_{t_0}$ differs by only a few per cent. from $T_t$). Equation (6) can now be rewritten, so that $p_t$ can be calculated directly from it,

$$p_t=p_i\left(\frac{2}{\gamma_0+1}\right)^{\frac{\gamma_0}{\gamma_0-1}}\left\{1+\frac{3\alpha T_i(\gamma_0-1)}{2(\gamma_0+1)^2}\right\},\quad .\quad (8)$$

since $p_i$, $T_i$, and the other factors are known.

*The Graphical Method of Determining* $T_t$ *exactly.*

During adiabatic expansive flow in a nozzle the velocity of the gas at the throat is equal to the velocity of sound in the gas at the throat. This relationship enables an equation to be formed connecting the throat acoustic velocity $A_t$ (ft./sec.) and the "heat drop" or decrease of enthalpy (C.H.U. per lb.) between the inlet and throat, *i. e.*, numerically

$$A_t^2=2gJ\int_{T_t}^{T_i}c_p dT,\quad .\quad .\quad .\quad .\quad .\quad (9)$$

or, from (2) and (4),

$$\left\{RT_t+\frac{R^2T_t}{J(a+bT_t+cT_t^2)}\right\}$$
$$=2J\left\{\left(a+\frac{R}{J}\right)(T_i-T_t)+\frac{b}{2}(T_i^2-T_t^2)+\frac{c}{3}(T_i^3-T_t^3)\right\},$$
$$.\quad .\quad .\quad (10)$$

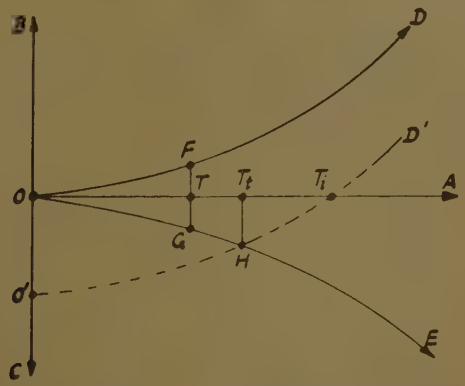
an equation from which $T_t$ is not very easily determined. The graphical method solves equation (10) exactly, and is illustrated in fig. 2.

*Description of the Graphical Method.*

OA is a rectangular axis along which is marked a uniform scale of absolute temperature with zero at O. OB and OC are axes along which the same uniform scale of heat energy (C.H.U. per lb.) is marked upwards and downwards respectively from a common zero O.

OD is a curve of enthalpy connecting OA with OB, while OE is a curve of "heat equivalent of acoustic velocity energy" connecting OA with OC. The construction of the curves OD and OE will be made clear by

Fig. 2.




considering the point T on the temperature axis. Let the absolute temperature at this point be T °C. The point F lies in the enthalpy curve.

The ordinate TF represents the enthalpy (C.H.U. per lb.) at T °C. and is calculated from

$$[TF]=\int_0^T c_r dT=\left(a+\frac{R}{\bar{J}}\right)T+\frac{b}{2}T^2+\frac{c}{3}T^3. \quad . \quad (11)$$

G is a point in the acoustic velocity energy curve. The ordinate TG represents the heat equivalent of the acoustic velocity energy (C.H.U. per lb.) at temperature T, and is given by

$$[TG]=\frac{A^2}{2g\bar{J}}=\frac{RT}{2\bar{J}}\left(1+\frac{R}{\bar{J}(a+bT+cT^2)}\right). \quad . \quad (12)$$

A number of values of the absolute temperature are selected and the two curves plotted.

The curve O′D′ is a movable one, and is obtained by tracing in ink upon a sheet of celluloid the curve OD which has already been drawn. The left-hand edge of the celluloid sheet coincides with the axis BOC. The sheet may be slid downwards to suit the problem, the left-hand edge remaining of course in BOC.

The temperature $T_t$ at the throat of the nozzle is then determined very simply, and equation (10) solved by the following geometrical step.

*Use of the Method.*

Let the temperature of the gas at inlet to the nozzle be represented by the point $T_i$ (fig. 2). The celluloid sheet is lowered until the curve O′D′ passes through $T_i$. A vertical line $HT_t$ drawn from H, the point of intersection of O′D′ and OE, to the temperature axis gives the temperature $T_t$ at the throat of the nozzle for adiabatic expansion.

The absolute pressure $p_t$ at the throat is now fully determined from (5):

$$p_t = p_i \left\{ \frac{T_t}{T_i e^{\alpha(T_i - T_t) + \beta(T^2 - T_t^2)}} \right\}^{\frac{1}{\gamma_0 - 1}}, \qquad . \quad (13)$$

thus completing the determination of the throat conditions.

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XXXI. *General Form of a Resonance Curve.* *By* Hikosaburo Ataka, *Meidi College of Technology, Tobata, Japan* *.

IN a network consisting of any number of linear impedances, connected in any manner whatsoever, and any number of generators of the same frequency, K. Spangenberg † has recently proved an interesting theorem.

The locus of any current or voltage in the system will be a circle, as any one self-impedance is varied so that its locus is a straight line in the complex plane.

Let $\dot{I}$ be a current through any branch of the network,

* Communicated by the Author.

† Proc. I. E. E. xxiv. pp. 652–662 (April 1936).

and $x$ a scalar representing the variable self-impedance. Then, following his notations, we shall have the equation

$$\dot{I}=\frac{\dot{L}x+\dot{M}}{\dot{P}x+\dot{Q}}, \quad \ldots \ldots \quad (1)$$

where $\dot{L}$, $\dot{M}$, $\dot{P}$, and $\dot{Q}$ are complex numbers depending upon circuit constants of the network and E.M.F.'s impressed.

If the absolute value of the current is plotted against the variable self-impedance in the rectangular coordinates, then we shall have a curve, which may be called a resonance curve in comprehensive meaning. Thus the general form of the resonance curve in the alternating network will be given by the equation

$$I=\left|\frac{\dot{L}x+\dot{M}}{\dot{P}x+\dot{Q}}\right|=\sqrt{\frac{L^2x^2+2\widehat{L\dot{M}}x+M^2}{P^2x^2+2\widehat{P\dot{Q}}x+Q^2}}, \quad \ldots \quad (2)$$

where L, M, P, and Q are the absolute values of the complex numbers $\dot{L}$, $\dot{M}$, $\dot{P}$, and $\dot{Q}$ respectively and $\widehat{L\dot{M}}$, $\widehat{P\dot{Q}}$ the scalar products of the corresponding complex numbers, that is, the sum of the product of real parts and that of imaginary parts.

It can easily be proved that both numerator and denominator of the fraction in the square root of (2) are always positive for all real values of $x$ from $-\infty$ to $+\infty$. In order to see the properties of the curve in detail, we shall transform (2) into the form

$$I=\frac{L}{P}\sqrt{1+\frac{2ax'}{x'^2+2bx'+c}}, \quad \ldots \ldots \quad (3)$$

where

$$x'=x+k,$$

and

$$\left.\begin{aligned} k&=\frac{1}{2a}\left(\frac{M^2}{L^2}-\frac{Q^2}{P^2}\right),\\ a&=\frac{\widehat{L\dot{M}}}{L^2}-\frac{\widehat{P\dot{Q}}}{P^2},\\ b&=\frac{\widehat{P\dot{Q}}}{P^2}-k,\\ c&=k^2-2\frac{\widehat{P\dot{Q}}}{P^2}k+\frac{Q^2}{P^2}. \end{aligned}\right\}$$

Between these constants there is an important relation. Since the function $x'^2+2bx'+c$ is obtained by the linear displacement with respect to $x$, from the function $x^2+2\frac{\widehat{PQ}}{P^2}x+\frac{Q^2}{P^2}$, which is always positive, the former is again always positive for all real values of $x'$ from $-\infty$ to $+\infty$, and its discriminant is, thus, negative.

$$b^2-c<0, \quad \text{or} \quad c>b^2.$$

The constant $c$ is always positive and greater than $b^2$.

(1) The asymptote of the curve is found by putting $x'=\infty$ or $x'=-\infty$, each of which gives a straight line parallel to the $x$-axis, that is,

$$I=\frac{L}{P}.$$

(2) The extreme values of I with respect to the variable $x'$ are given by the consideration of a function

$$y=\frac{2ax'}{x'^2+2bx'+c}. \quad \cdots\cdots \quad (4)$$

The first and the second differentials of $y$ with respect to $x'$ are as follows :

$$\frac{dy}{dx'}=\frac{-2a(x'^2-c)}{(x'^2+2bx'+c)^2},$$

$$\frac{d^2y}{dx'^2}=\frac{4a(x'^3-3cx'-2bc)}{(x'^2+2bx'+c)^3}.$$

The first differential vanishes when $x'=\sqrt{c}$ or $x'=-\sqrt{c}$. For $x'=\sqrt{c}$ we have

$$\frac{d^2y}{dx'^2}=\frac{-a}{\sqrt{c}(\sqrt{c}+b)^2},$$

which shows that

$$\frac{d^2y}{dx'^2}<0 \text{ for } a>0,$$

$$\frac{d^2y}{dx'^2}>0 \text{ for } a<0.$$

Thus in general there are two extreme values in the resonance curve. The maximum $I_{max.}$ and the minimum $I_{min.}$ of the current are as follows :

For $a>0$,

$$I_{max.} = \frac{L}{P}\sqrt{1+\frac{a}{\sqrt{c}+b}} \text{ when } x=\sqrt{c}-k,$$

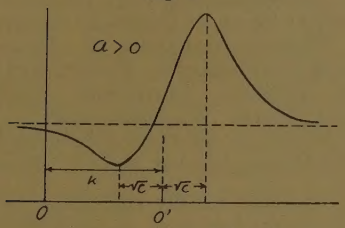
$$I_{min.} = \frac{L}{P}\sqrt{1-\frac{a}{\sqrt{c}-b}} \text{ when } x=-\sqrt{c}-k;$$

and for $a<0$,

$$I_{max.} = \frac{L}{P}\sqrt{1+\frac{-a}{\sqrt{c}-b}} \text{ when } x=-\sqrt{c}-k,$$

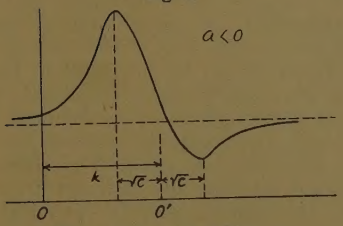
$$I_{min.} = \frac{L}{P}\sqrt{1-\frac{-a}{\sqrt{c}+b}} \text{ when } x=\sqrt{c}-k.$$

Fig. 1.




Resonance curve BA-type.

Fig. 2.




Resonance curve AB-type.

Now we can draw a resonance curve which is shown in fig. 1 or in fig. 2. Thus we have two kinds of resonance curve according to the sign of $a$. It may sometimes be convenient to call the curve in fig. 1 a resonance curve BA-type and that in fig. 2 a resonance curve AB-type. In a simple series resonant circuit we can usually observe

only a part of the curve BA-type, while in a simple parallel resonant circuit a part of the curve AB-type. However, in coupled resonant circuits it is very usual to observe the whole part of the curve BA-type or AB-type.

In conclusion, the writer wishes to express his deep appreciation to Prof. Kaduo Okada of this College, for his valuable advice.

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## XXXII. *Notices respecting New Books.*

*Biological Effects of Radiation. Mechanism and Measurement of Radiation, Applications in Biology, Photochemical Reactions, Effects of Radiant Energy on Organisms and Organic Products.* Edited by Professor Benjamin M. Duggar, with the cooperation of Janet Howell Clark, Kenneth S. Cole, Farrington Daniels, Gioacchino Failla, Charles Packard, and Henry W. Popp. [Vol. I., pp. x+676; Vol. II., pp. vii+677.] (McGraw-Hill Publishing Company, Ltd., Aldwych House, London, W.C. 2. Price 70*s*.)

IF these two volumes merely represent, as stated in the Preface, a by-product from one of the activities of the Committee on Radiation the total achievement of this body must be of quite extraordinary magnitude. The subject of the effects of radiation on living matter and vital processes is vast and diversified, by reason both of the considerable choice of radiation quality and of the endless variety of the biological material. Work in this field is beset with difficulties; on the physical side these are mainly concerned with the control and measurement of wave-length and intensity, and on the biological side with the isolation and measurement of the effects. Nevertheless research has been pursued with great and growing activity, although not always, it must be admitted, with the help of adequate physical knowledge or with the caution and judgment which is so essential in the interpretation of biological observations. It is obvious, therefore, that the task of surveying the extensive literature which has accumulated is one of peculiar difficulty. Its extent is sufficiently indicated by the fact that the bibliography includes well over four thousand references, and the range of topics covered is so large that it is not possible to enumerate them. Even so, it has been found necessary to exclude some

which might have been regarded as falling within the terms of reference, such as primarily clinical or therapeutic results, practical considerations relating to plant production, spectroscopic analysis of tissues etc., problems of vision, and so forth.

It need scarcely be said that the performance of a task such as this is quite beyond the competence of any one man. Actually some forty workers have collaborated in the undertaking, under the general guidance of the editor, Professor Duggar, assisted by a small committee. Each chapter is written by a specialist and is complete in itself. Whilst necessarily sacrificing continuity of treatment, this plan has the important advantage of permitting an authoritative and critical discussion of each topic. Much of the ground covered is so debatable that the contributors' views will not always be acceptable to their fellow experts. That is inevitable, and does not detract from the value of the book. The alternative, a colourless recital of all the published results, would have been of little more value than a mere bibliography. Such criticisms as are expressed appear to be informed and free from undue bias, and there is a general realization, expressed or implied, of the importance of a careful scrutiny of the method of investigators before accepting their conclusions. As a typical instance, it is pointed out that a good deal of work in connexion with the effects of ultra-violet radiation has been vitiated by inadequate control of other factors, such as temperature, total radiation intensity, visible and infra-red radiation.

Although, as has been said, any detailed discussion of the contents is out of the question, a brief reference to several of the chapters may be permissible. That dealing with the measurement and application of visible and near-visible radiation, by F. S. Brackett, is not only the longest but certainly one of the best in the book. Besides a very clear and comprehensive account of the characteristics and methods of measurement of the radiation it includes a great deal of information concerning sources and filters which many physicists as well as biologists will find most useful. The chapter on the problem of mitogenetic rays, by A. Hollaender, also calls for special mention as a really valuable discussion of a very perplexing situation. It merits the careful consideration of every worker, and especially of every intending worker in this field. The chapter on short electric wave radiation, by G. M. McKinley, may be particularly commended as a very sound and helpful contribution to a subject which is attracting increasing attention. Finally, Professor N. J. Reed's article on the statistical treatment of some biological problems will go far to meet the need which many biologists

feel for expert guidance in handling and interpreting their results.

The Editor and the Publication Committee are to be heartily congratulated on their achievement. They may rest assured that these volumes will be classed as indispensable in biological libraries and laboratories. They are admirably produced, and, although expensive, cannot be said to be dear.

*Tables of Physical and Chemical Constants and some Mathematical Functions.* By G. W. C. Kaye and T. H. Laby. Eighth Edition. (Longmans, Green, and Company. Price 14*s*.)

The first edition of the Kaye and Laby Tables, almost exactly a quarter of a century ago, was hailed with pleasure and recognized with relief as filling an important gap. The tables have become an almost necessary part of the book equipment of most laboratories.

Compared with the earlier editions the present eighth edition presents only minor differences and additions from its predecessor of twenty years ago—but these changes in content make the tables much more useful, since they include so many up-to-date references.

Naturally in a book of such modest size no individual worker can expect to see included everything he would like, but there are just two omissions which should be mentioned.

Why not, for example, in that excellent table of isotopes on page 156, give information about abundance? This could easily be done without unduly complicating the table. One looks in vain for electron stopping power information. There is a rough—and still useful—law which has been known for about twenty-five years.

There seem to be no serious mistakes or omissions in these well-produced tables—and it is good to see thicker and better quality paper used in their production. They may be thoroughly recommended once again, even at the rather high price of fourteen shillings.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]